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TRANSLITERATION

There is no ideal system of transliterating Russian; each has its advantages and disadvantages. For the translation of *Geokhimiya* we have chosen the system used by *Chemical Abstracts*, partly because of its wide acceptance by other journals and partly because of certain advantages in alphabetization of names. The principal differences between this system and others in common use are as follows:

Russian	Chem. Abs.	Others
Х	kh	h
Ц	ts	tz
Щ	shch	sch
Ю	yu	iu
Я	ya	ia

THE ABSOLUTE AGE DETERMINATION OF THE PRECAMBRIAN OF THE BALTIC SHIELD

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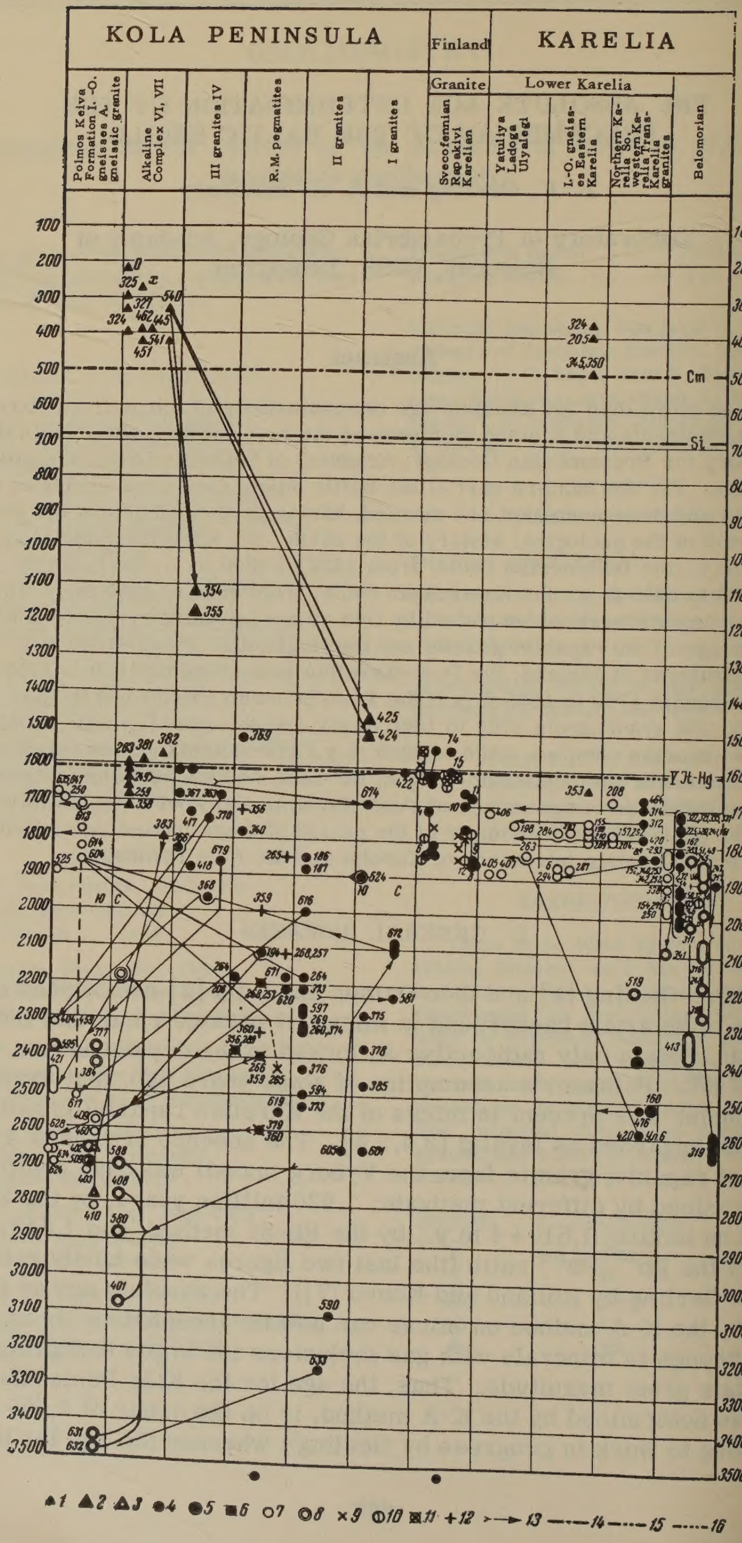
Laboratory of Precambrian Geology, Academy of
Sciences, USSR, Leningrad

Abstract

ata on more than 240 absolute age determinations of micas from Karelia, Kola Peninsula and Finland by means of the K-A-method, obtained in the ratory for Precambrian Geology, Academy of Sciences USSR, are given in rticle. For the eastern part of the Baltic Shield four large cycles of sedi- ation and metamorphism are marked, having proceeded before the Protero- period of the geological history of the earth: the Karelian cycle from 1500 80 m.y.; the Belomorian cycle, from 1830 to 2000 m.y.; the Saamian cycle, 2200 to 2400 m.y.; the Katarchean cycle, from 2820 to 3480 m.y. The or- movements were accompanied by five or six intrusive cycles of acid mag- The age of the rapakivi granite and the Hoglandian epoch—1640 m.y., the f intrusions of Finland; the Post-Karelian (postorogenic 1650 to 1750 m.y. ynorogenic 1760 to 1860 m.y.); the Post-Svionian (postorogenic 1550 to m.y. and synorogenic 1760 to 1860 m.y.); and the age of granite intrusions Belomorian complex (1900 to 2000 m.y.) are reliable values established ree methods (the potassium—argon, the lead, and the rubidium—strontium). he coincidence of age values of Post-Karelian and Post-Svionian intrusions s the question about the unity of the period of these intrusions of Finland he Post-Karelian intrusions of Karelia and the Kola Peninsula.

I. GENERAL REMARKS

After Gerling [1] and then Damon and Kulp [2] established the nce of an argon background in micas, it became clear that these rals contain only radioactive A, locked in the crystal lattice, in of K^{40}. Polkanov's assumption of some years ago, that excess A magma was present in micas of the Karelian rapakivi granite, d be regarded as invalid [3,4,5,6]. The absence of excess A in e of rapakivi granite from the Vyborg massif was also confirmed termined by different methods: 1,620 million years, by the K-A od on biotite; 1,610 ± 4 m.y., by the Rb-Sr method; and 1,642 ± 100 by the $Pb^{207}:Pb^{206}$ ratio (the last two figures were kindly relayed K. Gerling by Holland and Kouvo [7]). The absolute age as deter- d by the K-A method on micas can now be accepted as not exces- although in minerals with gas inclusions the argon background ttain great magnitude. Thus, the age for the Kola Peninsula , as determined by the K-A method, is on the order of 6,000 m.y., rding to work in progress by Gerling); whereas the age for beryls


KOLA PENINSULA
Finland
KARELIA
Polmos Kelva Formation I.-O. gneisses A. gneissic granite
Alkaline Complex VI, VII
III granites IV
R.M. pegmatites
II granites
I granites
Granite
Svecofennian Rapakivi Karelian
Lower Karelia
Yatuliya Ladoga Ulyalegi
I.-O. gneisses Eastern Karelia
Northern Karelia So. western Karelia Trans-Karelia granites
Belomorian
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
2000
2100
2200
2300
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2500
2600
2700
2800
2900
3000
3100
3200
3300
3400
3500
Cm
Si
Y Jt-Hg
▲1 ▲2 △3 ●4 ●5 ■6 ○7 ◎8 ×9 ⊕10 ▣11 +12 →13 14 15 16

n Mt. Beryl (U.S.A.) is as high as 5,000 and 4,000 m.y., according ata of Damon and Kulp [2] which we processed.

According to many accumulated data, Precambrian micas show a able loss of A, due to many geologic causes. For instance, the age roup III granites from the Kola Peninsula, which reaches 1,980 m.y. *), decreases to 1,110 and 1,180 m.y. at the contact with Paleozoic heline syenites (541 and 540) which are 330 and 410 m.y. old respectively. Granites of group I, underlying the Keiva formation (674), 1,700 m.y. old. However, a boulder of the same granite from a glomerate of the Keiva formation (524) is 1,900 m.y. old. In the t instance, the granite of group III contains aegirine-augite, proed by fenetization; in the second, granite of group I is migmatized ounger microcline granite.

A reliable control in such cases is the age determination for the e formations by the Sr and Pb methods, which decrease divergences he A-derived values. This is well illustrated by the ages of rapakivi nite, post-Karelian, and Svecofennian granites of Finland; the Beloian granites of Karelia; and rare-metal pegmatites of the Kola insula (Fig. 1).

The examples cited demonstrate that in geologically contemporanebiotites, those with the largest A^{40}/K^{40} ratio show the best age cidence with values determined by the Pb and Rb-Sr methods. Redless of these difficulties, we are determined to prove that radioogy in its present state "has a right" to set forth its premises in mating the geologic age of Precambrian formations.

ures in parentheses are sample numbers in Gerling's notebook.

---

1. Scheme of the age relationships in the Kola Peninsula, Karelian, and sh formations, from data by the potassium-argon (1-8), rubidium-stron-(9) and lead methods (10). 1—alkalic granites, syenites and nepheline sye-; 2—alkaline-earth granites, altered by alkalic rocks; 3—gneisses, altered kalic metasomatism; 4—alkaline-earth granites, groups I, II, III, IV; 5—es of group I granite from Keiva suite conglomerates; 6—granites, by the and Rb-Sr methods; 7—metamorphosed, supracrustal rocks; 8—metamord, migmatized supracrustal rocks; 9—granites-pegmatites, by the rubi-strontium method; 10—granites-pegmatites, by the lead method; 11—granby the lead and rubidium-strontium method; 12—granite, by the K-A methr which different ages were obtained with the Rb-Sr methods (number 9 his number); 13—arrows indicate reaction of a given granite or nepheline e with granite or supracrustal rocks, including migmatization; 14—age of ambrian (Kolm); 15—age of the Sinian (Sn) from glauconites of the Sinian tions of China; 16—ages of the Yotnian (It) and Hoglandian (Hg) Rapakivi es.

Conventional Abbreviations

I, VI and V - granite groups, IV and VII - complex alkalic granites, syeand nepheline syenites. R. M. - rare-metal, T. Kar - Trans-Karelia, outhern Polmos suites, N - northern Polmos suites, Su - suite, I.-O. - re, A - Archean.

Accordingly, the objective of "classical geology" should include above all a careful consideration of the radiogeologic values of the absolute age of Precambrian formations, accepting them as "tentative in some cases, and as "firmly established" in the others. "Classical geology" can no longer ignore these values, even though being utterly novel, they may run contrary to certain well-established opinions. Th thesis, an essentially new one, was formulated in our paper given at th International Geophysical Conference, Ottawa (Canada), in September 1957, and is the subject of this paper [18].

II. REVIEW OF AGE AND GEOLOGIC DATA

2. Figure 1 presents over 240 of our determinations of absolute ag for micas from Karelia, Kola Peninsula, and Finland by the K-A meth about 10 of our determinations of the age of micas by the Sr method; a

Table 1. Kola Peninsula and Karelia Paleozoic Intrusions (K-A method)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant*	Age in years using constan
345	Biotite from vein rock	Northern Karelia, Telyachii Is.	475	512
350	Biotite from monchiquite veins	Northern Karelia, Ovechii Is.	480	518
325	Biotite from turjaite	Kola Peninsula, Cape Turii, Kuznavolok	270	294
327	Biotite from ijolite	Kola Peninsula, Cape Turii	315	340
324	Biotite from micaceous ijolite dike	Kola Peninsula, Cape Turii	365	393
	Phlogopite	Northern Karelia, Vuoriyarvi	352	380
205	Vermiculite	Northern Karelia, Vuoriyarvi	373	402
462	Mica	Kola Peninsula, Afrikanda	362	39
451	Mica	Kola Peninsula, Afrikanda	395	42
445	Mica	Kola Peninsula, Seblyavrskii Massif	355	38
540	Nepheline syenite (sample from pebble)	Kola Peninsula, Kontozero	386	41
541	Nepheline syenite (sample from pebble)	Kola Peninsula, Kontozero	308	33
17	Feldspar	Kola Peninsula, Khibinskii Massif	280	30

*$\lambda_K = 6.02 \cdot 10^{-11}$ yr^{-1}; $\lambda_\beta = 4.9 \cdot 10^{-10}$ yr^{-1}

**$\lambda_K = 5.50 \cdot 10^{-11}$ yr^{-1}; $\lambda_\beta = 4.72 \cdot 10^{-10}$ yr^{-1}

Table 2. Karelian Karelia
(K-A method)

No. of deter- ations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
	Iron formation (Lower Proterozoic?)			
	Biotite from schist	Western Karelia, Gimoly	1740	1860
284	Biotite from biotite schist	Western Karelia, Bolshoe Lake	1660	1770
293	Biotite from pegmatite, cutting across iron formation	Western Karelia, Kostomuksha	1710	1820
294	Biotite from magnetite-biotite schist, interbedded with basalt conglomerate series	Western Karelia, Kostomuksha	1760	1880
	Ladoga formation (Lower Proterozoic)			
88	Muscovite from vein, cutting andalusite schists of Ladoga formation	Southwestern Karelia, Vakhavayarvi Lake	1710	1820
98	Biotite from porphyroblastic biotite schist	Southwestern Karelia, Northern Ladoga Area, Impiniemi Peninsula	1640	1750
12	Muscovite from granite, cutting across Ladoga schists	Southwestern Karelia, Northern Ladoga Area	1620	1730
14	Muscovite from granite, cutting across gabbrodiabase	Southwestern Karelia, Northern Ladoga Area	1590	1700
53	Biotite from granodiorite	Southwestern Karelia, Northern Ladoga Area, Kaalamo	1670	1790
54	Biotite from pegmatite granite, cutting Ladoga formation	Southwestern Karelia, Northern Ladoga Area, Latva-syurya	1520	1630
20	Muscovite from pegmatite granite, cutting Ladoga formation	Southwestern Karelia, Northern Ladoga Area, Matkaselka	1640	1760
	Pyrite formation (Lower Proterozoic)			
7	Biotite from biotite schist	Eastern Karelia, Onda River	1740	1860
7	Biotite from quartz-biotite-amphibole schist	Eastern Karelia, Parandovo	1650	1760

Table 2. (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
286	Biotite from mica-schist	Eastern Karelia, L. Voronya	1650	1760
199	Biotite from schist	Northern Karelia, Khizovara	1640	1750
155	Muscovite from schist	Northern Karelia, L. Vincha	1630	1740
209	Biotite from biotite schist	Northern Karelia, L. Kukasozero	1680	1790
210	Biotite from polymictic conglomerate cement	Northern Karelia, L. Kukasozero	1660	1770
208	Biotite from phyllite	Northwestern Karelia, L. Kautisyarvi	1580	1690
204	Biotite from mylonite	Northwestern Karelia, L. Nivayarvi	1690	1800
157	Muscovite from schist	Northwestern Karelia, L. Nyukhchyarvi	1660	1770
292	Biotite from mica-schist	Northwestern Karelia, L. Yulin-Kursuyarvi	1660	1770
406	Quartz-sericite schist (pebble sample)	Southwestern Karelia, Northern Ladoga Area, Yalonvaara	1600	1710
468	Biotite from granite	Southwestern Karelia, Northern Ladoga Area, M. Yanisyarvi	1490	1600
423	Biotite from quartz-feldspar veins, cutting lower Karelia rocks, and related to the Kartashovskiy Massif (lower Karelia) granites	Southern Karelia, Kartashi V.	1250	1340
371	Biotite from microcline granite, cutting lower Karelia rocks, underlying Yatulia rocks	Southern Karelia, Kartashi V.	1510	1620
		Yatulian formation (Middle Proterozoic)		
405	Sericite schist (quartzite conglomerate cement)	Central Karelia, Segozero, L. Makon-Saari	1750	1870
407	Sericite schist (pebble sample)	Southwestern Karelia, L. Yanis-Harvi, Cape Korkeaniyemi	1750	1870
		Pegmatite dikes, migmatites (Lower Proterozoic - Archean?)		
263	Muscovite from pegmatite	Southern Karelia, Ulyalegi	2430	2590

Table 2. (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
263	Biotite from schist	Southern Karelia, Ulyalegi	1710	1820
163	Muscovite from pegmatite	Southern Karelia, Ulyalegi, Brusnichnoe	2290	2430
42	Muscovite from pegmatite	Southern Karelia, Ulyalegi, Brusnichnoe	2430 without isotopes	2590
82	Muscovite from pegmatite	Southern Karelia, Ulyalegi, Brusnichnoe	2380	2530
123	Biotite from schist	Southern Karelia, Ulyalegi, Brusnichnoe	1540 1560	1650 1670
476	Muscovite from pegmatite in gneissic granites	Western Karelia, Bolshozero	2360	2510
160	Muscovite pegmatite particles in polymictic (basaltic conglomerate formation in iron-ore deposits)	Western Karelia, Sukozero	2390	2540
518	Muscovite from pegmatite	Southern Karelia, Koinary, Yurkostrov	2580	2750
519	Biotite from migmatite	Southern Karelia, Yustozero	2050	2190
298	Biotite from granite, cutting across gabbro-syenites of the Eletozero intrusion	Northern Karelia, Eletozero	1620	1720
353	Biotite from syenite of the Eletozero intrusion	Northern Karelia, Eletozero	1570	1670

15 determinations by the Pb-Sr and A methods, performed by Kakhma, Kouvo, and Holland on Finnish granites (Kouvo and Holland, personal communication, 1957; Kouvo [7]).

Above the 600 m.y. line (the age of the Cambrian [8]) and above the 680 m.y. line (the age of the Sinian as determined by us on glauconite from the Sinian deposits of China) there lies an age region of Permian nepheline rocks of Oslo (Norway), 225 m.y. old; the Kola Peninsula, 280 to 430 m.y. old; and Karelia, 370 to 520 m.y. old (Table 1). In addition to establishing this Paleozoic epoch of alkalic intrusions (280 to 520 m.y. old) our radiogeologic work indicates a Precambrian epoch 1,660 to 1,800 m.y. old which is prior (?) to the rapakivi granite intrusion, comprising the alkalic granite-syenites and nepheline-syenites of the Kola Peninsula and Karelia (Table 2).

No geologic formations for the Precambrian interval of 500 to 1,620 m.y. have been radiogeologically established in the Kola Peninsula and Karelia. Certain age values within this interval are associated with rejuvenated granites of group III. However, the possibility of this Precambrian age for certain rocks should not be ruled out (basic intrusions, Rybachii-Kildin formation, etc.).

On the Scandinavian peninsula, the following minerals fall in this ag interval: orthoclase and muscovite (Norway), 895 ± 5 and 965 ± 5 m.y. old, respectively, and bröggerite, 865 and 880 m.y. old—all associated with Gothokarelids; cleveite (Norway), 1,090 m.y. old and fergusonite (Sweden), 1,005 m.y. old—both associated with Svecofennids.

Thus, if the Proterozoic boundary is drawn between 1,000 and 1,500 m.y. no formation of Proterozoic age has been recognized in Finland, Karelia, or on the Kola Peninsula, for the rapakivi granite and the upper and lower Karelian formation are older than 1,620 m.y. and should be assigned to the uppermost Archean.

No Proterozoic formations younger than 1,500 to 1,600 m.y. have been recognized in the Ukrainian shield, where the youngest are rapakivi granites 1,750 m.y. old, nor in the Canadian shield where the late Keweenawan intrusions are now assigned to a late Huronian-early Keweenawan orogeny, with an age of 1,700 ± m.y. [9]. Evidently, the problem of the lower Proterozoic boundary must be reviewed in the light of these new data.

3. Platform formations of the upper Karelian include, according to K. O. Kratts, the Yotnian-Hoglandian and rapakivi granites whose age is reliably determined by three methods, as 1,640 m.y. The same age should be assigned to the Hoglandian deposits of Hogland Island, with extrusions of quartz porphyry; and also probably to gray quartzitic sandstones of the Onega region, pierced by dolerites and granosyenites. The age of these grano-syenites, as computed from feldspar is 1,200 + 25% or 1,500 m.y. Thus these rocks are younger than the rapakivi granite, which makes it possible to assign them to the Yotnia (Table 3).

The middle Karelian, according to Krotts, includes the Yatulian in which are sericite schists from Karelia 1,710 to 1,870 m.y. old. Krott admits that this age value is somewhat exaggerated because of the presence of clastic feldspar and mica in the schists.

Lower Karelian supracrustal formations of Karelia are from 1,690 to 1,890 m.y. old. The younger division, in Karelia, is 1,690 to 1,790 m.y. old, according to Krotts (Ladoga, Bolshozero, Parandovo, Vorone Khizovar, Vinch, Kukasozero, and southwestern Karelia formations), whereas the lower division is 1,820 to 1,880 m.y. old (Ulyalegi, Kostomuksha, Gimola, Onda formations). These values, however, are not distinguishable from the age of the Yatulian.

Table 3. Kola Peninsula
(K-A method; *Rb-Sr method)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
		Lower Archean (Svionian)		
410	Biotite from biotite gneiss	Voronya River	2650	2820
403	Biotite from biotite gneiss	Porkozero region, left bank of Voronya River	2550	2710
460	Biotite from biotite gneiss	Sulnguraz Mt., left bank of Voronya River	2460	2620
409	Biotite from biotite gneiss	Porkozero, left bank of Voronya River	2410	2570
618	Biotite from biotite gneiss in syenite-migmatite	Sulnguraz Mt., left bank of Voronya River	2580 2510	2750 2670
625	Biotite in biotite-bearing amphibolite (xenolith in granite-gneiss near the northern contact with the Polmos formation	Chankushveiv Mt., right bank of Voronya River	2700 2710	2880 2890
580	Biotite in biotite-bearing amphibolite (xenolith in granite-gneiss near the northern contact with the Polmos formation	Chankushveiv Mt., right bank of Voronya River	2700 2710	2880 2890
		Oligoclase granite gneiss, group I		
385	Biotite from oligoclase granite-gneiss	Voronya River	2320	2470
378	Biotite from oligoclase granite-gneiss	Vintras Mt., left bank of Voronya River	2220	2370
375	Biotite from granite-gneiss	Oarekuayv Mt., left bank of Voronya River	2150	2290
601	Biotite from diorite-gneiss	L. Repyavr	2490	2650
581	Biotite from plagiogranite (xenolith in microcline granite, group II)	Kedikpakh Mt., left bank of Voronya River	2080 2130	2220 2270
422	Biotite from oligoclase granite-gneiss (xenolith in microcline granite, group III) rejuvenated	Lyavozero	1500	1610

Table 3. Kola Peninsula
(K-A method; *Rb-Sr method) (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
425	Biotite from oligoclase granite-gneiss (near Paleozoic nepheline syenite intrusion) rejuvenated	Kontozero	1370	1460
424	Muscovite from oligoclase granite-gneiss (near Paleozoic nepheline syenite intrusion) rejuvenated	Kontozero	1410	1510
Microcline granites, group II (migmatite forming)				
408	Biotite from plagio-microcline granite	Voronya River, Dyavolov threshold	2600	2770
372	Biotite from plagio-microcline granite	Porkozero, left bank of Voronya River	2230	2380
509	Biotite from granite-gneiss	Ruchei Postnyi, right bank of Voronya River	2520	2680
588	Biotite from microcline granite	Tsutskyavriok River, right bank of Voronya River	2390 2430	2650 2690
401	Biotite from plagio-microcline granite	Shumbeir River region, left bank of Voronya River	2880	3060
Migmatites from microcline granites, group II				
631	Biotite from migmatite	Voronya River, Bolshie threshold	3225	3440
632	Biotite from migmatite substratum	Voronya River, Bolshie threshold	3260	3480
633	Biotite from pegmatite, related to granite migmatization, group II	Voronya River, Bolshie threshold	3060	3250
384	Granite - migmatite, group II (pebble sample	Porkozero, left bank of Voronya River	1910	2040
590	Biotite from group II pegmatite, migmatizing oligoclase granite-gneiss (gr. I)	Chankushveiv Mt., right bank of Voronya River	2910	3100
Pegmatites from microcline granites, group II				
671	Biotite from pegmatite (cutting Archean gneiss)	Sulnguraz Vil., left bank of Voronya River	2020 2050	2150 2180

Table 3. Kola Peninsula
(K-A method; *Rb-Sr method) (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
619	Muscovite from pegmatite, group II, cutting Archean migmatites	Pellapakhk Vil., right bank of Voronya River	2390	2540
260	Biotite from pegmatite dike	Voronya River, shore of L. Sukhy	2190	2330
374	Biotite from pegmatite dike	Kyarchveiv Mt., southern Polmos formation	2180	2320
269	Muscovite from pegmatite dike	Voronya River, southern Polmos formation	2140	2280
373	Biotite from pegmatite dike	Porkozero, southern Polmos formation	2070	2210
594	Biotite from pegmatite separation in granite-migmatites, group II	Oarekuaiv Mt.	2370	2430
376	Biotite from pegmatite separation in granite-migmatites, group II	Chuvichyavopakhk Mt.	2280	2430
597	Biotite from pegmatite along amphibole lens contact, near northern contact with Polmos formation	Chankushveiv Mt., right bank of Voronya River	2125	2270
		Iron formation and cross-cutting granites		
617	Biotite from biotite gneiss	Olenegorsk Vil.	2380	2530
616	Muscovite from pegmatite	Olenegorsk Vil.	1880 1850	2000 1970
615	Biotite from tectonic biotite gneiss	Kola Fjord, western shore of Vydraruchie	1600	1710
614	Biotite from mica granite-schist	Bay of Murmansk	1700	1810± 50 2130± 170*
613	Biotite from biotite schist	Titorka River	1620 1660	1730 1780
612	Biotite from plagiogranite	Polyarnoe Vil. Ekaterininskii Is.	1960 2000	2090 2130
605	Muscovite from pegmatite	Kola Fjord, northern shore of Gryaznoi Bay	2490	2650
604	Biotite from mica schist	Kola Fjord, Cape Pinogorii	1725	1850

Table 3. Kola Peninsula
(K-A method; *Rb-Sr method) (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
603	Biotite from granite-gneiss	Tuloma River, left bank, to the north of Murmasha	1665	1785
		Polmos formation		
404	Biotite from biotite gneiss	Shumveiv Mt., western limit of Polmos formation	2170 2175	2310 2320
459	Biotite from biotite schist (in conglomeratic rocks)	Shumveiv Mt., western limit of Polmos formation	2160	2300
421	Biotite from biotite granite gneiss	Kontozero region, central part of polmos formation	2300 2370	2450 2510
595	Biotite from gneiss in tourmaline pegmatitic granite	Leshaya Mt.	2330	2380
634	Biotite from biotite gneiss in the base of the Polmos formation	Chokkvara Mt., left bank of Voronya River	2500 2490	2660 2650
624	Hornblendic rock	Ruchei Postnyi near Okhmylk Mt.	2530	2690
593	Biotite from schist (formed by the action of Polmos aplitic rocks, group III(?), on amphiboles)	Leshaya Mt.	2400	2660
		Rare-metal pegmatites		
266	Muscovite from rare-metal pegmatite in the Polmos formation	Okhmylk Mt., vein No. 3	2250	2400
194	Muscovite from rare-metal pegmatite in the Polmos formation	Okhmylk Mt., vein No. 6	1990	2120
360	Muscovite from rare-metal pegmatite in the Polmos formation	Vasin-Mylk Mt., vein No. 18	2200	2340±50 2600±200*
206	Muscovite from rare-metal pegmatite in the Polmos formation	Vasin-mylk Mt., vein No. 18	2060	2200

Table 3. Kola Peninsula
(K-A method; *Rb-Sr method) (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
268	Muscovite from rare-metal pegmatite in the Polmos formation	Vasin-mylk Mt.	1980	2100 2190± 180*
357	Muscovite from rare-metal pegmatite in the Polmos formation	Vasin-mylk Mt.	1980	2110 1880± 150* 2000
359	Muscovite from rare-metal pegmatite in the Polmos formation	Polmos Tundra	1880 1820	2400± 190* 1940
264	Muscovite from rare-metal pegmatite	L. Bolshoi Lapot	2040	2180
265	Muscovite from rare-metal pegmatite	L. Bolshoi Lapot	1710 1700	1830 1830 2450+190*
Pegmatites, cutting across the Polmos formation				
620	Muscovite from pegmatite (non-rare-metal) cutting across Polmos formation amphibolites	Okhmylk Mt.	2130 2160	2276 2300
379	Muscovite from pegmatite (non-rare-metal) cutting Polmos formation gneiss	Shumveiv Mt.	2440	2600
Pegmatite dikes with spodumene				
340	Muscovite from pegmatite with spodumene	Kolmozero	1670	1780
356	Muscovite from pegmatite with spodumene	Kolmozero	1610	1740 2380± 190*
389	Muscovite from pegmatite with spodumene	Kolmozero	2200	2350 2270± 180*
369	Muscovite from pegmatite with spodumene	Soldat-mylk Mt.	1440	1530
Microcline granites, group III				
363	Biotite from microcline granite, cutting across Polmos formation	Kontozero	1580	1690

Table 3. Kola Peninsula
(K-A method; *Rb-Sr method) (Continued)

No. of determinations 1	Petrography 2	Location 3	Age in 10^6 years, using old constant 4	Age in 1 years, using ne constant 5
364	Biotite from an analogous microcline granite from another massif (having been subjected to the activity of Paleozoic nepheline syenites)	Kontozero	950	1010
365	Biotite from the same granite	Kontozero	1100	1180
370	Muscovite from pegmatite dike in greisenized granite, cutting across Polmos formation	Porosozero	1640	1754
368	Muscovite from greisenized tourmaline microcline granite, cutting across Polmos formation	Porosozero	1860	1980
417	Muscovite from microcline granite	Eastern Lyavozera	1605	1725
418	Muscovite from microcline granite	Eastern Lyavozera	1740	1860
678	Biotite from microcline granite (postkinematic intrusion)	L. Litsa (northern contact of Polmos-Porosozera formations)	1530	1640
646	Biotite from microcline granite	Kontozero	1510	1620
370	Biotite from pegmatite in group III granite	Kontozero	1640	1750
	Pegmatites from group III granites			
679	Muscovite from group III pegmatite	Eastern Lyavozera	1740 1720	1860 1840
367	Muscovite from group III pegmatite	Lagedovka River	1580	1680
366	Biotite from group III pegmatite	Lagedovka River	1710	1830
	Alkalic syenites			
382	Pegmatite from alkalic syenite (pebble sample)	Sulnguraz Mt.	1400	1500 1800
383	Alkalic syenite (pebble sample)	Porkozero	1240	1330 1566

Table 3. Kola Peninsula
(K-A method; *Rb-Sr method) (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
	Pegmatites, cutting across granulite formation			
296	Muscovite from greisen, included in quartz-molybdenite vein, cutting across granite	Yauri-ioki River	1670	1790
186	Muscovite from greisenized granite, cutting àcross granulite	Yauri-ioki River. (Yuvvoaiv Mt.)	1720	1840
187	Muscovite pegmatite dike, cutting Archean gneiss	Yauri-ioki River. (Yuvvoaiv Mt.)	1760	1880
	Keiva formation - basement gneisses			
524	Biotite from oligoclase-granite pebble in basalt conglomerate	Western Keivy	1765	1890
525	Biotite from cement of basalt conglomerate	Western Keivy	1760 1780	1880 1900
674	Biotite from biotite-oligoclase granite, which is overlain by the Keiva suite basalt conglomerate (with large amounts of microcline)	L. Leiyavr, Ilyukoro Mt.	1590 1600	1690 1700
	Keiva formation			
647	Biotite from mica gneiss	Western Keivy	1580	1690
635	Biotite from garnet-biotite gneiss	Western Keivy	1590	1700
650	Muscovite from muscovite schist	Keivy, Berezovaya	1580	1690
	Pegmatites from alkalic granites of Keivy			
358	Muscovite from pegmatite dike in alkalic granites	Keivy, Serpovidnyi Range	1610	1720
259	Muscovite from pegmatite dike in alkalic granites	Western Keivy, Pestsovaya Mt.	1570	1680
270	Muscovite from pegmatite dike in alkalic granites	Central Keivy, Vargelurta tundra	1570	1680

Table 3. Kola Peninsula
(K-A method; *Rb-Sr method) (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 1 years, using ne constan
1	2	3	4	5
355	Muscovite from pegmatite dike in alkalic granites	Keivy, Serpovidnyi Range	1540	1650
249	Muscovite from pegmatite dike in alkalic granites	Keivy, Pestsovaya Mt.	1530	1640
263	Mica from quartz-ilmenite vein	Keivy, Serpovidnyi Range	1500	1610
381	Biotite from nepheline syenite	Gremyakha-Vyrmes pluton, Cape Eriginovyi	1500	1600
682	Biotite from nepheline syenite	Gremyakha-Vyrmes pluton	1575	1675
529	Biotite from nepheline syenite	Gremyakha-Vyrmes pluton	1510	1610
531	Biotite from nepheline syenite	Kuliok massif, southern Keivy	1470	1510

Granites that pierce the Ladoga formation are 1,600 to 1,820 m.y. old. Pegmatite cutting the Kostomuksha formation is 1,820 m.y. old. It follows that the age of these two formations must be over 1,820 m.y old. The Ulyalegi schists, cut by a pegmatite 2,590 m.y. old, must be still older, but are rejuvenated to 1,820 m.y., because of the loss of argon.

The lower Karelian Keiva Formation, on the Kola Peninsula, is 1,690 m.y. old. The age for a conglomerate cement from this formation (1,900 m.y.) may be exaggerated because of some clastic materia in it. A boulder of group I granite, from the same conglomerate, is 1,900 m.y. old (Table 3).

Alkalic granites, cutting the Keiva formation, have an age of 1,610 to 1,720 m.y.; the associated alkalic syenites are 1,570 to 1,800 m.y. old. Consequently, the true age of the Keiva formation is over 1,720 t 1,800 m.y. but not over 1,900 m.y. (the conglomerate boulder).

A parallel determination by both Sr and Pb methods is necessary t pinpoint the age of the supracrustal Karelian and post-Karelian granit

It has been radiogeologically established that alkalic granosyenites of the Kola Peninsula are contemporaneous with the Gremyakha-Vyrmes nepheline-basic rocks of that peninsula—1,650 m.y. old--and of Eletozero, Karelia—1,680 m.y. old.

Thus on the basis of radiogeology Karelian orogenic movements on the Kola Peninsula led to the formation of the folded Keiva belt and to

Table 4. Finland
(K-A method)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
574	Biotite from Svecofennian, synorogenic granodiorite	Krakvaaka, Maalakhti	1740 1560	1840
575	Biotite from granite-late synorogenic	Khirvilampi	1500	1610
576	Biotite from granite-Svecofennian, late orogenic	Perniya	1700	1820
577	Biotite from granite-Svecofennian, late orogenic	Tuuliainep, Lemi	1520 1580	1630 1690
543	Muscovite from pegmatite	Viitaniemi, Eroyarvi	Not determined	
544	Muscovite from pegmatite, penetrating through Svecofennian schists	Mittkarr Kamio	1710	1830
545	Biotite from granite-Svecofennian, post-orogenic	Onas Porvo region	1440 1450	1540 1550
578	Biotite from albite-biotite rocks - Karelian, early synorogenic	Riikonkoshi, Kittilya	1740	1860
573	Biotite from granodiorite-Karelian, synorogenic	Saariyarvi, Siomussalmi	1720	1840
579	Biotite from granodiorite-Karelian, synorogenic	Kilpisyarvi, Enontekio	1540 1590	1650 1700
542	Biotite from granite-Karelian, late synorogenic	Khetta, Enontekio	1610	1720
546	Biotite from granite-Karelian, late orogenic	Maariavara, Kaavi	1720 1690	1840 1810
547	Muscovite from pegmatite, penetrating granulite formation	Passeltavara	1720	1840
548	Biotite - muscovite from granite - rapakivi, Karelian, post orogenic	Uto Korpo	1440	1540
	Biotite from rapakivi pegmatite*	Vyborgskii massif	1520	1620

*Specimen from the laboratory collection of the Geology of the Precambrian, Acad. Sci. USSR; the other specimens are from the collections of the Finnish Geological Institute, Helsinki.

the intrusion of alkalic granites whose trend is traced farther northwest across the peninsula to the international border. In this connection we note the occurrence of alkalic syenites in the area of Voronya River and in the Chagveuaiv, between Zapadnaya Litza and Titovskaya Rivers, where they cut the ancient Archean basement [10]. The tectonic movement of that age may have been the cause of the rejuvenation of Archean basement rocks (see age of the iron-ore formation, below). Southwest of this tectonic zone, faults originated in rigid Archean blocks, in intermontane areas, and in geanticlinal uplifts of the Karelids. These faults served as vents for intrusive complexes of basic nepheline plutons in Gremyakha-Vyrmes [11] in the Kola Peninsula, and Eletozero in Karelia. The same age should be assigned to some of the mafic subalkalic dikes at the northwestern edge of the Kola Peninsula [12].

4. Post-Karelian granites, according to our K-A and Finnish Pb^{207}-Pb^{206} and Rb-Sr determinations, are 1,650 to 1,845 m.y. old. These figures range between 1,760 and 1,850 m.y., thus coinciding wit the age of the post-Karelian granites of Karelia.

The age of the Svecofennian granites of Finland is 1,550 to 1,860 m.y., as determined by our K-A and Finnish K-A, Pb, and Rb-Sr methods. The figures fall into two groups: one between 1,550 and 1,64 m.y., the other between 1,750 and 1,850 m.y.

A correlation of the ages for the Svecofennian granites of Finland (by three methods), 1,550 to 1,860 m.y., and the post-Karelian granite of Finland, Karelia, and Kola Peninsula, shows close coincidence. In addition, the age of the granite group (1,550 to 1,640 m.y.) coincides with that of the rapakivi granite group (1,600 to 1,650 m.y.), whereas the age of the 1,750 to 1,850 m.y.-old granite group coincides with tha of the post-Karelian granites (1,750 to 1,850) and Karelia (1,600 to 1,820 m.y.). Unfortunately, there are no age determinations for the supracrustal Svionian and Karelian of Finland as yet (Table 4).

The coincidence in ages for the Svecofennian granites of Finland and the post-Karelian granites of Finland, Karelia, and Kola Peninsul suggests their geological synchronism. This leads us to the question of age identity for the Svecofennids of Finland and the Karelids of Karelia and Kola Peninsula. Recall that Sederholm [13] in 1932 and Sudovikov after the Patriotic War assigned the Ladoga formation to th Archean, based on geologic data, whereas Backlund [15] assigned mos of Finland and Karelia to the Karelids. Now armed with the new methods and data of radiogeology, we may return to this problem.

Another problem may be posed, that of similarity in the radiogeologic age of rapakivi granite intrusions in the south and central part o the Baltic shield (1,550 to 1,650 m.y.), and post-Karelian alkalic gran syenites—nepheline syenites of the Kola Peninsula (1,610 to 1,710 m.y

In this connection, it is interesting to note that the rapakivi granite are younger than the Yatulian of Karelia and Finland, just as the Keiv and Imandra-Varzuga formations of the Kola Peninsula are older than

Table 5. Western White Sea
(K-A method)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
	A. Gneisses and migmatites of the White Sea complex			
154	Biotite from garnet-biotite gneiss	Karelia mine, Kipatvaraka	1850	1970
271	Biotite from garnet-biotite migmatized gneiss	Karelia mine, Perti-varaka, vein No. 1	1840	1960
256	Biotite from garnet-biotite migmatized gneiss in contact with pegmatite dike	Karelia mine, Pertivaraka, vein No. 1	1810	1930
158	Biotite and muscovite from a garnet-biotite layer in two mica gneiss from amphibolites	Pongomskii Bay, Mramornyi Is.	1730	1840
252	Biotite from kyanite-garnet-biotite gneiss	Chkalova mine, 20/m from "8 Marta" pegmatite stock	1760	1880
253	Biotite from kyanite-garnet gneiss	Chkalova mine, in the "8 Marta" contact vein	1710	1830
338	Biotite and muscovite from fine-grained biotite gneiss, weakly migmatized	Knyazhegubskii Gulf, cliff at the mouth of Knyazhnaya Bay	1800	1920
393	Muscovite from fine-grained, highly migmatized biotite gneiss	Knyazhegubskii Gulf, cliff at the Mouth of Knyazhnaya Bay	1740	1860
337	Biotite from biotite granite-gneiss	Kandalakshskii Bay, Irinin Is.	1810	1830
336	Biotite from biotite-plagioclase-microcline granite-gneiss	Kandalakshskii Bay, Irinin Is.	1720	1840
335	Biotite from granite, cementing fragments of amphibole (agmatite	Kandalakshskii Bay, Afanaska cliff	1880	2000
340	Biotite from strongly migmatized amphibole-biotite gneiss (finely layered migmatite)	Kandalakshskii Bay, Burichek Is., 20 m. from gabbro-norite massif	1750	1870
342	Biotite from biotite crystal segregation near assimilated fragment of amphibole	Kandalakshskii Bay, Burichek Is., 2 m. from gabbro-norite massif	1750	1870

Table 5. Western White Sea
(K-A method) (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
341	Biotite from biotite-amphibolite fragment in highly migmatized amphibole-biotite gneiss	Kandalakshskii Bay, Burichek Is., 2 m. from gabbro-norite massif	1970	2100
B. White Sea complex vein formation Pegmatoid veins (synorogenic)				
97	Biotite from fine-grained pegmatoid dikes with layered apophyses in amphibole-biotite gneiss	Chupinskii Gulf, Cape Kartash	1850	1970
283	Muscovite from fine-grained gneissic pegmatite dikes in biotite granite-gneiss	Northwest shore of White Sea, Cape Sharapov, Tryasova Bay	1700	1820
Pegmatite dikes (late synorogenic)				
57	Muscovite from pegmatite, plagioclase-muscovite vein in kyanite-granite-biotite gneiss	Malinovaya varaka mine, vein No. 2	1800	1920
8/32	Muscovite from pegmatite dike in kyanite-garnet-biotite gneiss	Tedino mine, Slyudovaraka, vein No. 32	1790	1910
255	Muscovite from pegmatite dike in kyanite-garnet-biotite and garnet-biotite gneisses	Karelia mine, pertivaraka, vein No. 1	1750	1870
254	Biotite from pegmatite stock, in kyanite-garnet-biotite gneiss	Chkalova mine, "8 Marta" vein	1740	1860
51	Biotite from pegmatite dike in garnet amphibolites	Velikaya salma, Kindomys peninsula, vein No. 2	1720	1840
49	Biotite from pegmatite dike, in gabbro-amphibolites, included in finely-bedded migmatites and anatexites	Panfilova varaka mine, Bolshaya Panfilova vein	1720	1840
103	Biotite from pegmatite dike, cutting across pegmatite dike (Sple. 97)	Chupinskii Bay, Cape Kartash	1830	1950

Table 5. Western White Sea
(K-A method) (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
	Quartz-carbonate veins			
156	Muscovite from quartz-carbonate-muscovite veinlet in granite-gneiss	Keretskii archipelago, cliff south of Ileikin Is.	1740	1860
232	Biotite from quartz-carbonate-biotite veins in gabbro-amphibolites	Northwest shore of White Sea, Cape Sharapov, Tryasova Bay	1720	1840
319	Biotite from quartz-carbonate-biotite veins in meta-gabbro-diabase	Keretskii archipelago, Vichennaya Is. cliff	2430 2510	2590 2670
	Vein granites			
334	Biotite from fine-grained plagioclase-microcline granite dike, cutting across migmatites	Kandalakshskii Bay, Demenikha Is.	1890	2020
333	Biotite from fine-grained plagioclase-microcline granite dike, cutting across migmatites	Belikaya Salma, Kuzokotskii Peninsula	1800	1920
	C. Post-orogenic pegmatites			
159	Biotite from pegmatite dike, cutting amphibole-bearing meta-gabbro diabase dike	Gridino, Giblova cliff	1810	1930
162	Biotite from pegmatite dike, cutting across block of migmatized amphibole gneiss and amphibolites	Gridino, Lesovataya cliff	1680	1790
161	Biotite from pegmatite dike, cutting across amphibolites alternating with marble layers	Kandalakshskii Bay, Suprotivnyi Is.	1650	1770
225 231	Muscovite from pegmatite dike, cutting across a meta-gabbro-diabase block, of the late orogenic group	Kandalakshskii Bay Valetov Is.	1640 1620	1750 1730

Table 5. Western White Sea
(K-A method) (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 1 years, using ne constan
1	2	3	4	5
241	Biotite from pegmatite stock in meta-gabbro diabase of the late orogenic group	Pongomskii Bay, Okhlyabinin Is.	1660	1770
320	Pink muscovite, lithium bearing Pegmatite dike in meta-gabbro-diabase	Loukhskii region, L. Pizemskoye	1630	1740
321	Green muscovite, lithium bearing			
322	Biotite		1610	1720
Granites (post-Karelian - N. G. Sudovikov, 1937)				
212	Biotite from biotite-hornblende (with garnet) porphyroblastic granite	Pongomskii Bay, Pongomnovolok Peninsula	1780 1770	1900 1890
244	Biotite from biotite hornblende granite-gneiss	Kem River, Poduzhemskii threshold	1770 1740	1890 1860
Granite-gneiss and migmatites from the eastern side of Vicheunaya cliff				
183	Biotite from migmatized biotite granite-gneiss xenolith in a mass of meta-gabbro-diabase, of the late orogenic group	Keretskii archipelago, Vichennaya Is. cliff	2230 2190	2280 2330
245	"	"	1720	1840
311	"	"	1890	2020
318	Biotite from biotite formation near contact with migmatites of the marginal zone of the meta-gabbro-diabase	"	2120	2260
246	Biotite from biotite granite-gneiss, 20 cm. from contact with meta-gabbro-diabase block	Keretskii archipelago, Vichennaya Is. cliff	1860	1980
247	Biotite from biotite granite-gneiss, 200 cm. from contact with meta-gabbro-diabase	"	1730	1850

Table 5. Western White Sea
(K-A method) (Continued)

No. of determinations	Petrography	Location	Age in 10^6 years, using old constant	Age in 10^6 years, using new constant
1	2	3	4	5
248	Biotite from migmatized biotite granite gneiss near meta-gabbro-diabase block (layered migmatite)	Keretskii archipelago, Vichennaya Is. cliff	2040 1950	2180 2080
316	Biotite from granitized biotite gneiss near meta-gabbro-diabase block (shaded migmatite)	"	1770	1890
317	Muscovite and biotite from plagioclase-microcline granite gneiss (anatexites) near meta-gabbro-diabase	"	1780 2430	1900 2590
319	Biotite from quartz-carbonate veins in meta-gabbro-diabase	"	2510	2670

the alkalic granites. In turn, the Yatulian of Karelia and Finland is not cut by post-Karelian granites, i.e., the Yatulian is younger than the latter, just as the Keiva formation is younger than the post-Karelian granites [16]. Further refinement of the radiogeologic ages for all these formations would take us a long way toward understanding the Precambrian geology of the east part of the Baltic shield.

5. The next youngest formation, according to radiogeologic data, is the Belomorian of Karelia, which extends into the south Kola Peninsula. Supracrustal Belomorian gneisses are 1,800 to 2,100 m.y. old. The considerable range of these values is related to the degree of migmatization. A portion of these age values coincides with the age for the base of the Karelian, but most of them exceed it by some 200 m.y. (Table 6).

The synorogenic and postorogenic pegmatites and granites, according to Shurkin, are 1,720 to 2,020 m.y. old. Their age partly coincides with that for the post-Karelian granites, but most of them are much older. The age of the older Belomorian pegmatites, determined by the K-A method, coincides with that for uraninite from the Chkalov vein, found to be 1,950 m.y. as determined by Pb^{207}/Pb^{206}, Pb^{206}/U^{238}, Pb^{207}/U^{235} ratios (Sabotovich; paper presented at the VII Session of the Commission for the Absolute Age Determination of Geologic Formations,

1958). In this case, the younger age limit for pegmatites, if it is ma
more precise by other methods, may coincide with the age of post-Karelian granites. Furthermore, the age data for granites led to the
belief that the supracrustal Belomorian formation cannot be younger
than 1,950 m.y.

Judging from geologic studies by Shurkin, the tin-ore exposures o
the Keret archipelago are of great interest, for a xenolith of an ancie
migmatite found there has an age of 1,840 to 2,330 m.y. The enclosi
metagabbro is 2,260 m.y. old. The metagabbro is migmatized, its ag
becoming successively younger, from 2,180 to 1,850 m.y. This rock
complex is cut by a biotite-quartz-carbonate vein, 2,590 to 2,670 m.y
of age. Shurkin regards the Belomorian gneiss complex as having
originated in a single migmatization process. In his opinion, the age
relationship as given is erroneous.

On the other hand, Sudovikov recognizes two migmatization epoch
in the Belomorian complex which, in his opinion, could correspond t
the above-mentioned ancient xenolith and vein. (The senior author a
concurs in this view.) This problem has great geological and metho
ological import, and should be given special consideration.

6. There are other instances of more ancient formations in Kare
Yustozero migmatites - 2,190 m.y. old; pegmatite pebbles from a co
glomerate underlying the Sukozero iron-ore formation - 2,390 m.y.
Bolshozero pegmatite which cuts the gneisses - 2,360 m.y. old; Ulya
pegmatite, cutting the schists - 2,590 m.y. old. These data suggest
presence of formations older than the Belomorian in the south part o
Central Karelia; special study is needed to clarify their geology (Fig

7. Let us turn to the iron formation of the Kola Peninsula which,
according to Polkanov [11], is Archean in age. Sederholm [13] appl
the name Lapponian to this formation and assigned it to the upper
Archean. Following a study by Mickol, Wahl [17] regarded this form
tion as Karelian in age (Table 4).

Specimens of the ore-bearing gneisses from the northern belt of
formation (collected by Polkanov) are 1,710 to 1,850 m.y. old. At th
same time, oligoclase granite of group I, which migmatizes this for
tion, is older—2,000 to 2,130 m.y. A pegmatite cutting the oligoclas
granites is still older, being 2,650 m.y. old.

The rare metal-bearing pegmatite which cuts the ore-bearing for
mation in the area of Lake Lapot has an age of 1,830 and 2,180 m.y.
the K-A method; 2,450 m.y. by the Rb-Sr method.

Gerling assigns this northern belt of ore-bearing gneisses to the
lower Karelian. However, the granites that cut it raise its age to 2,
and 2,650 m.y. Thus, the age of the ore-bearing formation probably
was lowered by post-Karelian tectonic movements whose zone, acco
panied by intrusions of alkaline grano-syenites, is located within the
northern belt of this formation.

Another specimen of mica gneiss from the southernmost Olenego
(Zaimandrov) iron belt is 2,530 m.y. old, whereas a pegmatite that c

Table 6. Precambrian of the Baltic Shield

Orogeny	Division	Regions	Magmatic and Supracrustal Complexes	Age (10^6 years)	
				Supracrustal formations*	Magmatic rocks
Hercynian and Caledonian 280-520 m. y.		Norway, Oslo Kola Peninsula Karelia	Nepheline intrusive complex " "		225 280-430 370-520
Gothokarelian 865-965 m. y.		Norway			895-965 863-880
Svecofennian 1000-1090 m. y.		Norway Sweden			1090-1050 1005
N. Karelia-Karelian 1830-2100 m. y.	Upper		Iotnian Rapakivi Hoglandian	1500 1620-1640	1500 1620-1640
	Middle	Karelia	Yatuliya - Karelia	1710-1870	
			Alkalic granites		1600-1740
			Alkalic syenites		1580-1800
			Alkalic nepheline syenites		1600-1680
		Karelia Kola Peninsula Finland	Granites post-Karelian		1620-1820
			Granites group III granites		1640-1870
			Granites post-Karelian post-orogenic		1650-1750
			Granites post-Karelian synorogenic		1760-1850
			Granites Svecofennian post-orogenic		1550-1660
			Granites Svecofennian synorogenic		1760-1860
	Lower {Upper Lower	Karelia Kola Peninsula Karelia	Keiva formation.	1690-1790 1680-1790 1820-1880	
III. Belmorian 1830-2100 M. Y.			Granites and pegmatites	1830-2100	1720-2020
II. Saaminian 2300-2700 M. Y.	Upper Lower		Poros formation Polmos iron formation	2300-2450 2600-2700	1700-2600
I. Catarchean 2820-3480 M. Y.	Upper Lower		Granites, migmatites	2820-3060 3440-3480	1840-3250

*Age of metamorphism

this formation is 1,970 to 2,000 m.y. old. (II granite group), both suggesting an older age for the ore-bearing formation.

8. The Polmos tundra formation, in the northeast of the Kola Peninsula, formerly thought to be of Karelian age, is now traced over 150 km and tentatively subdivided into two parts: an upper, essentially gneissic formation—the Poros formation—and a lower, essentially greenstone, gneissic formation—the Polmos proper. The Poros formation is 2,300 to 2,350 m.y. old; the Polmos—2,600 to 2,700 m.y. old. The Polmos formation contains newly discovered iron ore deposits, thus becoming the fourth ore-bearing belt, located to the north of the Kola fjord (the third ore-bearing region).

To the north and south of this Polmos and Poros belt, there lies a vast expanse of gneiss-granites and migmatites of granite groups I and II which contain a gneiss sequence and small bodies of gneisses similar to those of the Poros and Polmos formations. Correspondingly, the age determination for these rocks gives two groups of figures, 2,190 to 2,430 m.y., and 2,550 to 2,780 m.y. (Table 4).

The same region of gneiss development also contains other gneiss horizons and xenoliths of supracrustal rocks and their migmatites. Here granite groups I and II may likewise be differentiated into two groups, according to their age: very ancient ones, 2,820 to 3,060 m.y old, and some even older, 3,440 to 3,480 m.y. old. However, the geo ogy and distribution of these formations are still obscure.

9. Within the same area of gneiss-granite distribution, as well as the Polmos and Poros formations, normal calc-alkalic granites and granodiorites are present. These are petrographically separable int three groups. The most ancient of them, plagioclases and pegmatites of group I, are 1,700 to 2,650 m.y. old. Some of the youngest of thes were undoubtedly rejuvenated during their migmatization by granites of group III (underlying the Keiva formation) (Table 4).

Microcline granites and pegmatites of group II migmatize granite group I, and are from 1,840 to 3,250 m.y. of age. The only age determination was done on a specimen 1,850 m.y. of age, by the K-A meth and 2,450 m.y., by the Rb-Sr method. These divergent ages suggest some loss of A and a rejuvenation for a number of rocks of this grou

Group III of microcline granites has an age from 1,110-1,180 to 1,970 m.y. These granites cut the Poros formation. Their lower ag limit, 1,110 to 1,180 m.y., is associated with specimens from a conta with the Kontozero nepheline syenites, and is affected by A loss in fenitization. The same age group includes microcline pegmatitic gra ites that cut the granulites in the western Kola Peninsula, 1,790 to 1,880 m.y. of age.

In addition, a special group of rare metal pegmatitic granites is recognized; they cut the Polmos and Poros formations and the iron o bearing formation and are assigned an age of 1,530 to 2,600 m.y. (K-

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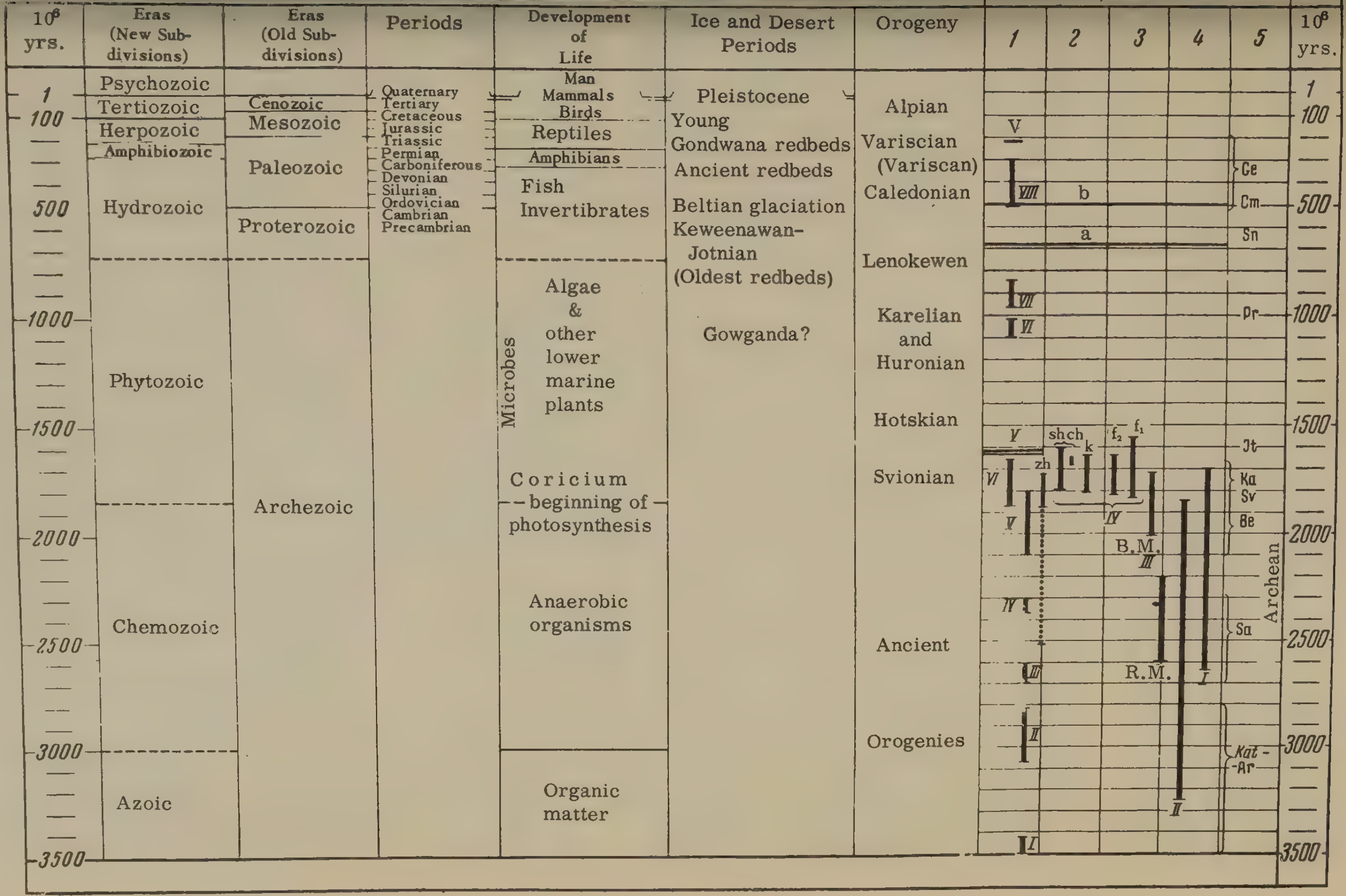
Fig. 2. Geochronological table according to P. Eskola, and absolute age of ge logical formations of the Baltic Shield according to the Laboratory of Precambrian Geology, Academy of Sciences, U.S.S.R.

First column: I, II—Katarchean (?) gneiss (Kat-A). III, IV—Saamian gneiss (V—Belomorian gneiss (Be). VI—Karelian gneiss (Ka-Sv). Zh—Iron ore formation, Kola Peninsula. V (horizontal line)—Jotnian, Hoglandian, Rapakivi (It). VI—Svecofennian pegmatite, Scandinavian Proterozoic (Pr). VII—Gothokareli pegmatites, Scandinavia. a (horizontal)—age Sinian (Sn). b (horizontal)—Cambrian (Cm). VIII—Groups of nepheline syenites, Kola Peninsula, Karelia, Osl (v).

Second, third, fourth columns: Granite intrusions of the Kola Peninsula, Kare (K) and Finland (F). I—First group; II—Second group; R.M.—Rare metal pegmatites; III—White Sea granites of Karelia; IV—F_1 Post-Karelian granites of Finland; F_2 Svecofennian granites of Finland; K—Post-Karelian granites of Karelia; Shch—Alkalic granites, syenites, nepheline syenites of the Kola Peni sula and Karelia.


10⁶ yrs.
Eras (New Sub-divisions)
Eras (Old Sub-divisions)
Periods
Development of Life
Ice and Desert Periods
Orogeny
1
2
3
4
5
10⁶ yrs.
1
100
500
1000
1500
2000
2500
3000
3500
Psychozoic
Tertiozoic
Herpozoic
Amphibiozoic
Hydrozoic
Phytozoic
Chemozoic
Azoic
Cenozoic
Mesozoic
Paleozoic
Proterozoic
Archezoic
Quaternary
Tertiary
Cretaceous
Jurassic
Triassic
Permian
Carboniferous
Devonian
Silurian
Ordovician
Cambrian
Precambrian
Man
Mammals
Birds
Reptiles
Amphibians
Fish
Invertibrates
Algae & other lower marine plants
Microbes
Coricium
beginning of photosynthesis
Anaerobic organisms
Organic matter
Pleistocene
Young
Gondwana redbeds
Ancient redbeds
Beltian glaciation
Keweenawan-Jotnian
(Oldest redbeds)
Gowganda?
Alpian
Variscian
(Variscan)
Caledonian
Lenokewen
Karelian and Huronian
Hotskian
Svionian
Ancient
Orogenies
V
VIII
b
a
VII
VI
V
shch
k
zh
f₂
f₁
VI
V
IV
B.M.
III
IV
III
R.M.
I
II
II
I
Ce
Cm
Sn
Pr
Jt
Ka
Sv
Be
Archean
Sa
Kat-Ar

method). Five determinations by the Rb-Sr methods gave an age of 2,200 to 2,600 m.y., raising the age for individual samples by 100 an 650 m.y.

It has not been geologically established, what relationship, if any, exists between these rare-metal pegmatites and granites. By their they may be assigned to either granite group I or II.

SUMMARY

10. The data cited support certain preliminary conclusions whic may have considerable bearing on the problem of Precambrian geol (Fig. 2).

a) Four major cycles of sedimentation and metamorphism are su gested by the Argon method of the absolute age determination for th eastern part of the Baltic shield (Kola Peninsula, Karelia and Finlan I:- Katarchean, with upper and lower stages (?). II - The Saamian, w two stages: 1 - Polmos formation with iron ore-bearing formation, 2 - Poros formation. III - The Belomorian (with one or two stages). IV - The Karelian with three stages: 1 (lower) Karelian; 2 (middle) Yatulian; and 3 (upper) Yotnian, Hoglandian. The orogenic movemen were accompanied by five or six intrusions of silicic magma, groupe as follows: I - Plagiogranite. II - Microcline granites and rare me pegmatites. III - Belomorian microcline granites. IV - Post-Svioni (?) granites of Finland. V - Rapakivi granite. VI - Alkalic granosyenites, nepheline syenites; all of a post-Karelian age.

b) All of these cycles of sedimentation, metamorphism, and intru sions terminated prior to 1,600-1,500 m.y. ago, i.e., prior to the Pr terozoic (taking the lower age boundary for the Proterozoic at 1,000 1,500 m.y.). However, in including the Karelian epoch of sedimentat metamorphism, and magmatism in the Proterozoic, the lower age li for the Proterozoic is pushed back to 1,800-1,900 m.y.

c) The age limits as given for the several cycles are mostly tent tive and require further study by the Pb and Rb-Sr methods. The reliable values, as determined by the three methods, are the followi rapakivi granite and the Hoglandian epoch—1,640 m.y.; post-Svionia intrusions of Finland: post-orogenic 1,650 to 1,750, synorogenic 1,7 to 1,850, and post-orogenic 1,550 to 1,660 and synorogenic 1,760 to 1,860 m.y. The coincidence of these values poses a question concer ing the identity of post-Svionian and post-Karelian intrusions of Fin with post-Karelian intrusions of Karelia and Kola Peninsula. An unavoidable corollary would be to unite them into a single Svecofennia or else post-Karelian intrusive epoch of group IV of the alkaline-ea granites.

Finally, the age of post-orogenic Belomorian granites, as determined by two methods, is 1,950 m.y.

d) One cannot fail to notice the long duration of the several perio of sedimentation, metamorphism, and especially of magmatism, as compared with those for the Paleozoic-Cenozoic eras of the geologic history of the earth. A refinement of the age values for metamorphic and magmatic cycles by the Sr and Pb methods will probably not only narrow these age limits but also lead to further and more detailed differentiation of the intrusive and sedimentary cycles.

Both the age figures and the geology suggest such a differentiation into 2 cycles for the Karelian rocks and for the Saamian rocks. For granite groups I and II, several cycles are suggested corresponding to the orogenic and metamorphic cycles.

One of us deems it partially possible to realize such a differentiation even now.

e) Further radiogeological studies may possibly succeed in establishing a Precambrian age for rocks younger than Yotnian and Rapakivi for the eastern part of the Baltic shield. However, reliable data are lacking, as yet.

For Scandinavia, we have cited the age data for the Gothokarelids based on 895 to 965 m.y., for orthoclase and muscovite from Norway (K-A method) and 865 to 880 m.y., for bröggerite from Norway. The age of the Svecofennids is based on: 1,090 m.y., for cleveite (Arendal) from Norway, and 1,005 m.y. for fergusonite (Iterbi) from Sweden (by the Pb method).

These age values for the Gothokarelids and Svecofennids of Scandinavia are lower by a factor of 1.5 than those for the rapakivi and post-Karelian and Svecofennian granites of Finland and Karelia, which suggests different ages for the three (two) cycles.

f) The nepheline rock complexes of Scandinavia, the Oslo area, are assigned to the Permian, with an age of 225 m.y.

The Paleozoic nepheline-basic intrusions of the Kola Peninsula and Karelia are dated somewhere between 280 and 520 m.y. A refinement of these values by the Sr and Pb methods may at the same time define several epochs of alkalic intrusions for that province.

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APPLICATION OF THE Ca METHOD IN THE ABSOLUTE AGE DETERMINATION OF SYLVITES

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Abstract

Parallel determinations of the sylvite age with the aid of the calcium and potassium-argon methods have been carried out. Radiogenic calcium was determined using the method of isotopic dilution, and the potassium content in sylvites was determined using the dipycrilamine method. Argon was isolated from the samples by melting sylvite in vacuum and was measured using the volumetric method. The results obtained show good preservation of radiogenic argon in samples not having been submitted to recrystallization. The age data for sylvites not recrystallized agree well according to the independent Ar^{40}/K^{40} and Ca^{40}/K^{40} ratios. The experiments have shown that the recrystallization of sylvite does not influence the data of the calcium method. The lesser migration capacity of calcium compared to argon makes it possible to determine the age of potassium salts with the aid of the calcium method even in the case of their complete recrystallization.

INTRODUCTION

The Ca method, based on β-decay of K^{40}, was first introduced by A. Holmes [1] as a potential method of absolute age determination. However, a practical realization of this method encountered great experimental difficulties, chiefly because of the insignificant content of radioactive Ca^{40} even in Ca-rich ancient minerals.

A method had to be devised for separating micro-quantities of Ca from large amounts of K, which is the material hindering mass-spectrometric determinations of Ca. Furthermore, the isotope composition of native Ca is 96.92% Ca^{40} isotope of nonradioactive origin, which greatly complicated the analysis and distorts its results.

SUBJECT AND GOAL OF THE INVESTIGATION

The Pb and Rb methods are inapplicable in the verification of A-method data and in the evaluation of the degree of conservation of radioactive A in sylvites. Accordingly, an application of the Ca method in obtaining comparative data by different methods was of interest. Sylvites are most appropriate for the application of the Ca method, as they contain large amounts of potassium and consequently perceptible amounts of radioactive Ca^{40}.

In the analysis, two specimens of white sylvite from bed ''B'' of the Verkhnekamensk formation (Mt. Berezniki) were used, and one from the Polovininsk drill hole (Irkutsk amphitheatre). The age of the Verkhnekamensk K-salts has been fairly well established as lower Permian (Kungur stage). Sylvite from the Polovininsk drill hole is found in 1.5-2 cm inclusions in a halite horizon from the Usol formation, Lena stage (Lower Cambrian).

Sylvite-bearing rock salt from the Polovininsk drill hole is obvious recrystallized; it is reasonable to assume that the sylvite in it is also recrystallized. We assumed that the A-method data would date the las recrystallization, whereas the true age of the sylvite could be established by the Ca method, from the Ca^{40}/K^{40} ratio. Similar results wer anticipated for the water-transparent recrystallized sylvite from a len in bed ''B'' of the Verkhnekamensk site. The second specimen was taken directly from bed ''B'' and consisted of coarse crystals of milky white non-recrystallized sylvite.

SEPARATION OF RADIOACTIVE CALCIUM FROM SYLVITE

Potassium hinders mass-spectroscopic determination of calcium; its ionization capacity is about 100 times greater than that of Ca. The peak of mass 39 is very large, even with negligible admixtures of K, a it is superimposed on the Ca^{40} peak whose intensity is further increase because of the K^{40} isotope. Consequently, it was imperative to achieve a practically complete separation of Ca and K in the specimens under study. Complete Ca separation was not necessary for its mass-spectrometric determination; however, because of a low content of radioactive Ca in sylvites, its loss in the process of analysis has to be minimized in order to avoid using excessive amounts of the original sample.

The method of fractional recrystallization with multiple reprecipitation of Ca in oxalate form, as applied by Inghram, Patterson, Brown, and Hess [2] to separate Ca from sylvite is protracted and complicated We experimented with a simpler method. The method was developed with pure salts; Ca^{45} isotope was used as a radioactive indicator to determine the source of Ca loss and the completeness of its separation Measurements were made with the ''B'' type installation having an end window counter.

The separation of Ca and K was most effective with ion-exchange resins; K:Ca ratios were 100:1 and 10,000:1, and the Ca yield 92%. A further K increase in samples (in order to approximate the natural K:Ca ratio in sylvite) led to an increase in the volume of the column, which lowered the Ca yield to 55-60%. Thus the necessity of a preliminary elimination of the bulk of K became obvious. To achieve that, we applied the method of ''salting-out'' of K by HCl. A sample containing 10 g of KCl and 0.007 g of $CaCl_2$* was dissolved in 30 ml of water, and heated to the solution point. Then concentrated HCl was added drop-by-drop until first crystals appeared, whereupon the solution was cooled slowly, decanted, evaporated to one-fourth of its volume, and the "salting-out" was repeated. After four precipitations, the solution containing about 1 g K was evaporated dry and its activity measured. For comparison, a similar sample was freed of K by the fractional recrystallization method.

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*A precisely measured amount of calcium chloride was added, whose content of Ca^{45} isotope was known, and the specific activity measured.

Table 1 gives a comparison of the two methods.

Table 1

	Fine crystallization	Salting-out
Content of KCl in evaporate residue, g	1.1	1.0
Total β-radiation of residue, with background correction, pulse/min.	153± 14	350± 22
β-radiation of residue, due to K^{40} and background, pulse/min.	110± 12	110± 12
β-radiation due to Ca^{45}, pulse/min.	43± 12	240± 12

As it appears from the table, the concentration of Ca in precipitation is six times greater than in the fractional recrystallization; the method is simpler and requires fewer operations.

A processing of the precipitate revealed β-activity due to the K present in it. Thus the bulk of K in samples was successfully separated, with hardly any loss of Ca.

The final separation of Ca from K was achieved by its triple reprecipitation as oxalate, with subsequent measurement of its β-activity. The Ca yield was 92.95%. In order to determine the degree of contamination by native Ca, the entire experiment was repeated on a sample containing 100 g of KCl and 0.1 mg of $CaCl_2$ enriched by Ca^{43} isotope.

The isotope content for the separated Ca does not differ from the original composition of a standard Ca^{43} solution, which suggests a lack of perceptible contamination by native Ca from the vessels and reagents. Traces of K in the separated Ca were so insignificant as not to affect the mass-spectrometric analysis.

Thus, the desalting method is simpler than the fractional recrystallization method, and is justified in the application to the soluble K salts; their K was virtually completely separated, whereas the Ca loss was only about 5-7%.

The degree of separation of radioactive Ca from large amounts of K may be judged from mass-spectrograms represented in Figs. 1 and 2, which show the spectrum of common Ca as compared with that for Ca obtained from recrystallized sylvite.

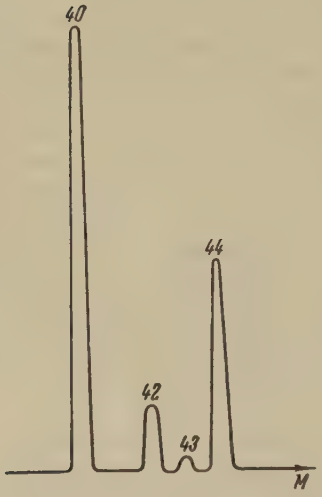

Fig. 1. Spectrum of natural calcium (the peaks of mass 42, 43, and 44 are enlarged 25 times).

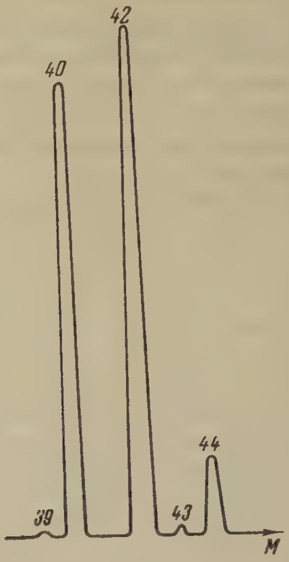

Fig. 2. Spectrum of calcium, isolated from sylvite, with an admixture of calcium enriched with Ca isotope (the peaks of mass 42, 43, and 44 are enlarged 5 times).

DETERMINATION OF RADIOGENIC CALCIUM BY THE ISOTOPE DILUTION METHOD

The isotopes of radiogenic Ca were analyzed with mass-spectroscope MC-2 m, by the single-ray method, with receiver's slits somewhat modified. The surface-ionization method was used in the measurements. Because of the comparatively low ionization capacity of C it had to be increased in order to achieve a steady ion current with small amounts of Ca.

We used a cathode of platinum-plated tungsten ribbon. The combination of high-yielding capacity of platinum surface and high-melting temperature of the tungsten base made it possible to intensify Ca ionization. The main advantage of this method is that even microgra amounts of Ca on the platinum-plated tungsten cathode emit a steady ion current lasting several hours, long enough for precision measurements.

The isotope-dilution method was used in the measurement of micr quantities of Ca, as proposed by Rittenberg [3] and described in detai by Inghram and others [4,5]. A Ca compound, enriched by Ca^{42} isoto was used for diluent.

The per cent relationship of Ca isotopes in the standard diluting solution was established by mass-spectrometry as follows: Ca^{40}, 27.4%; Ca^{42}, 68.9%; Ca^{43}, 0.3%; and Ca^{44}, 3.4%.

A quantity of diluent, measured with a micropipette (the concentration of solution was previously established by the weight method*), was added to the sylvite sample to be analyzed. The sample dissolved, and K was separated as before by desalting. The thrice reprecipitated calcium oxalate was dissolved in nitric acid. After the excess acid had been evaporated, the calcium nitrate was dissolved in several milliliters of water. This solution contained unknown amounts of native and radioactive Ca and a known quantity of Ca from the diluent, enriched by Ca^{42}.

In the method of isotope dilution, a loss of Ca is not critical, since it is proportional for all Ca isotopes. The quantitative content of radioactive and native Ca was computed from the following equations:

$$
\begin{aligned}
y + ax + bP &= \alpha \\
cx + dP &= \beta \\
ex + fP &= \gamma
\end{aligned}
$$

where x is the weight of native Ca in sample;
y is the weight of radioactive Ca^{40};
a is the atomic content of Ca^{40} in native Ca;
b is the atomic content of Ca^{40} in diluent;
P is weight of Ca in diluent;
d is atomic content of Ca^{42} in native Ca;
c is total content of Ca^{40} in sample;
α is atomic content of Ca^{42} in diluent;
β is total content of Ca^{42} in sample;
e, f, γ are analogous values for Ca^{42} isotope.

The mass-spectrometric experiments determined the ratios $\alpha:\beta:\gamma$. Table 2 gives the results of our mass-spectrometric determinations of radioactive Ca in three sylvite specimens.

The degree of contamination by native Ca was determined from equation $x = \dfrac{\frac{\gamma}{\beta} d - f}{e - \frac{\gamma}{\beta} c} P$, while the radioactive Ca content was determined from the equation: $y = \left(\frac{\alpha}{\beta} d - b\right) P - \left(a - \frac{\alpha}{\beta} c\right) x$.

It appears from the table that despite careful selection of specimens, the contamination by native Ca is fairly noticeable; for ancient sylvite, it exceeds the radioactive Ca content approximately by the factor of 10. However, this does not hinder the determination of radioactive Ca^{40} by the isotope dilution method.

A much more serious hindrance in the age calculation by these data is the indefiniteness of the $Ca^{40}:Ca^{44}$ ratio in native Ca, as first indicated by Ahrens [6].

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*In all experiments, we added 2 ml of diluent containing 161.6 mg of Ca.

The knowledge of the isotope composition of Ca, and more specifically precise data on the ratio of distribution of native Ca isotopes and masses 40 and 44 ($Ca^{44}:Ca^{40}$), are essential in the age calculation by the Ca method. The isotope content of native Ca was determined by Nier [7], White and Cameron [8], and later by Akishin, Panchenkov and others [9]. The data by those authors are given in Table 3; they illustrate the lack of precision in the determination of the $Ca^{44}:Ca^{40}$.

This forced us to measure the $Ca^{44}:Ca^{40}$ ratio in calcium oxide, which was accomplished with a mass-spectrometer having the ion source based on the surface ionization phenomenon, with results very close to those obtained by White and Cameron (Table 4).

An analysis of the measuring methods of Nier and White gives reason to regard the results of the latter as more reliable. Accordingly we used the value of $Ca^{44}:Ca^{40}$

Table 2. Mass-spectrometer Determination of Calcium from Three Sylvites by the Isotope Dilution Method

Description of mineral	Isotope composition of dilution				Amt. of sylvite, g	K, μg	Amt. of introduced Ca, μg	$\frac{\gamma}{\beta}$	$\frac{\alpha}{\beta}$	Content of radioactive Ca, μg	Contamination with natural Ca, μg	$\frac{Ca^{40}}{K^{40}}$	Age in million years
	Ca^{40}	Ca^{42}	Ca^{43}	Ca^{44}									
Water-transparent recrystallized sylvite from lens in stratum "B" (Upper Kam formation)	27.4	68.9	0.3	3.4	22.46	1382	161.6	0.122	5.2	168	391	0.121	228±7
Milky-white unrecrystalized sylvite from stratum "B" (Upper Kam formation)	"	"	"	"	14.04	871	"	0.168	6.8	106	654	0.121	228±7
Water-transparent sylvite from halite layer in the Usolskii suite (Polo-	"	"	"	"	[illegible]	[illegible]	"	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 3. Isotope Composition of Natural Calcium

State of calcium	Ca^{40}	Ca^{42}	Ca^{43}	Ca^{44}	Ca^{46}	Ca^{48}	Author
Metallic calcium	99.96± ?	0.64± ±0.010	0.145± ±0.004	2.06± ±0.06	0.0033± ±0.0006	0.185± ±0.0055	Nier
Calcium oxide	99.92± ±0.3	0.64± ±0.01	0.130± ±0.004	2.13± ±0.04	0.0032± ±0.04	0.180± ±0.001	White and Cameron
Metallic calcium	97.01± ±0.22	0.67± ±0.05	0.15± ±0.01	2.01± ±0.02	-	0.16± ±0.02	Akishin, Panchenkov et. al.

as determined by White, Cameron, and ourselves, in our further calculations.

DETERMINATION OF Ca AND A IN SYLVITES

The K content in sylvites was determined by the dipicrylamine method as described by Sverzhinskaya and Knipovich [10], and verified with radioactive tracers by Murina, Iskanderova, and Sprintsson [11]. The K content in all analyzed samples was over 51%, thus confirming the purity of the material.

Argon was extracted by melting the sylvite in a vacuum. The radioactive A content was determined by the volumetric method, with an installation for the microanalysis of noble gases, similar to that described by Gerling [12]. A mass-spectrometric analysis of A separated out of sylvite demonstrated its radioactive purity, so that the correction for air A did not exceed 4%.

Table 5 gives the results of analysis of two sylvite specimens from the Verkhnekamensk site, and of an ancient sylvite from the Polovinsk drill hole (Irkutsk amphitheatre).

The isotopic analysis of argon separated from sylvite was performed by A. V. Mattes with a MS - 2m mass-spectrometer.

The perceptibly smaller amount of A separated out of recrystallized specimens is of interest. This may be explained either by loss of the original argon, in recrystallization, or by its diffusion from the crystalline lattice of sylvite in the course of geologic time. However, the fair coincidence of the age of a nonrecrystallized specimen with the

Table 4.

The relationship of isotope distribution	Accord. to Nier	Accord. to White	Our calculations
Ca^{44}/Ca^{40}	0.0212± ±0.0006	0.0219± ±0.0004	0.0221± ±0.0004*

*This is the mean square error of our experiments.

prevailing geologic ideas suggests a lack of perceptible effect of argon diffusion, whose part in coarse-grained specimens (such as all three of ours) appears to be negligible.

The age calculations were done with the following values of K-decay constants: 1) $\lambda_\beta = 4.9 \cdot 10^{-10}$ year^{-1} which is the average for six of the more reliable measurements [Danilevich, 13]; 2) value of K-decay constant ($\lambda_k = 0.602 \cdot 10^{-10}$ year^{-1}) as obtained by Gerling [14].

The age of sylvites was computed from formulas:

$$\frac{mCa^{40}}{mK^{40}} = \frac{\lambda_\beta}{\lambda + \lambda_k}\left[e^{(\lambda_\beta + \lambda_k) \cdot t} - 1\right] \quad \text{Ca method}$$

$$\frac{mA^{40}}{mK^{40}} = \frac{\lambda_k}{\lambda_\beta + \lambda_k}\left[e^{(\lambda_\beta + \lambda_k) \cdot t} - 1\right] \quad \text{A method}$$

where mCa^{40} and mA^{40} are quantities of radioactive Ca and A in samples, in grams

mK^{40} is the K^{40} isotope content in samples, in grams
λ_β and λ_k are K-decay constants
e is base of natural ln
t is age in million years.

The last two columns of Table 6 show the results of the age computation, as done by us with the use of K^{40} decay constants (λ_β and λ_k), of the American workers. As shown on the table, the data for the non-recrystallized specimen coincide well, although they were obtained from independently arrived at ratios of A^{40}:K^{40} and Ca^{40}:K^{40} (Table 6).

These data attest the good preservation of radiogenic A in the non-recrystallized sylvite specimen. Considerable rejuvenation, as determined by the A method, takes place in the two recrystallized specimens, especially in the ancient sylvite.

It appears to us that the part of A diffusion is not too essential, and

Table 5. Age of Three Sylvites According to Data by the Argon Method

Location of sample	Description of mineral	Content of K, %	Amt., g	$K^{40}10^{-5}$ g/g	Content of atmospheric A, %	$A^{40}10^{-7}$ g/g	$\frac{A^{40}}{K^{40}}$	Age, in million years
Stratum "B," Upper Kam formation	Milky-white, non-recrystallized sylvite	51.7	10	6.20	0.3	8.85	0.0142	220
			10	"	0.1	8.41	0.0135	209
Lens in stratum "B," Upper Kam formation	Water-transparent recrystallized sylvite		10	6.16	4.0	6.18	0.0100	115
		51.3	15	"	2.0	5.81	0.0092	146
Polovininsk well, Irkutsk amphitheater	Water-transparent recrystallized (?) sylvite	51.1	2.53	6.13	2.5	5.74	0.0095	148

Table 6. Age of the Sylvites by the Calcium and Argon Methods

Mineral	Age in million years		Geologic age	Age in million years	
	with $\lambda_\beta = 4.9 \cdot 10^{-10}$ yr.$^{-1}$ and $\lambda_K = 0.602 \cdot 10^{-10}$ yr.$^{-1}$			with $\lambda_\beta = 4.7 \cdot 10^{-10}$ yr.$^{-1}$ and $\lambda_K = 0.55 \cdot 10^{-10}$ yr.$^{-1}$	
	$\frac{A^{40}}{K^{40}}$	$\frac{Ca^{40}}{K^{40}}$		$\frac{A^{40}}{K^{40}}$	$\frac{Ca^{40}}{K^{40}}$
Non-recrystallized sylvite from stratum "B," Upper Kam formation	215± 5	228± 7	Kungurian stage, Lower Permian	236	241
Recrystallized sylvite from lens in stratum "B," Upper Kam formation	150± 5	228± 7	"	165	241
Polovininsk well, Irkutsk amphitheatre	148± 10	620± 20	Usolsk suite Lensk stage, Lower Cambrian	162	660

we explain the "rejuvenation" of sylvite by the total loss of the original A in the process of recrystallization. On geologic considerations, such a recrystallization of both samples in the Jurassic is very probable. Thus the lower Paleozoic of the Irkutsk amphitheatre region is transgressively overlain by Jurassic deposits. Moreover, elements of salt tectonics are clearly noticeable in galena beds. It appears that the A method data suggest Jurassic as the time of the last recrystallization, which does not contradict geologic evidence.

It is very essential that the recrystallization of sylvites has no effect on the Ca method data. Consequently, the more restricted migration of Ca as compared with A makes it possible to determine the age of K-salts by the Ca method even in the event of their full recrystallization, which may turn out to be very important in the deciphering of the origin and geologic history of K-salt deposits.

The research in this direction will be continued on ancient K-salts from exploration drill holes, and it is our hope that new data would justify our assumption. Even if the Ca method is not likely to become popular, it may be a check for the A method in many instances. Presently its application is contemplated for the age determination of potassium micas (muscovites and lepidolites) from pegmatite veins.

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APPLICATION OF SULFUR ISOTOPE ANALYSIS IN THE STUDY OF THE UCHALA (SOUTH URALS) COPPER PYRITES

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Abstract

Sulfur isotope analysis has been used for ascertaining the genesis of minerals of the copper-pyrite Uchala deposit in the Southern Urals. The data indicate that the pyrite ores and the copper-zinc ores belong to different stages of ore formation. The similarity of the isotopic sulfur composition of pyrite of massive and impregnated ores bears witness to a common sulfur source for the solutions which formed them.

INTRODUCTION

Foremost among the controversial, still unsolved problems of the origin of copper pyrites of the Urals is that of the nature of qualitative heterogeneity of sulfide ores. Some investigators [1, 2], in developing the familiar thesis of Zavaritskii, regard this heterogeneity as a result of far-reaching processes of rearrangement of the ore substance, believing that the latter originally formed in a single stage. The others [3, 4] consider the uneven distribution of primary associations of minerals deposited from solutions during the several stages of the ore-forming process to be the basis of the qualitative inconsistency of ore. In the opinion of the latter, the metamorphic phenomena did nothing but complicate the interrelationship of mineral complexes of different age, affecting their structure and texture, but only locally changing composition.

The complexity of this problem called for new methods of solution. One of them was the determination of the sulfur isotope content for different generations of sulfides and sulfates, the components of ore mineral associations in the Uchala pyrite deposits of the southern Urals.

This ore site has been the subject of a comprehensive mineralogical study, the results of which enabled the authors to identify typical mineral associations and to collect a systematic series of specimens for analysis. Studies by the isotope analysis method were designed to corroborate the presence of various mineral associations in pyrite ores and to supply data on the development of processes of redeposition and addition or subtraction of matter during ore formation. The results of this study are the subject of the present paper.

It should be noted that some of our conclusions, which are based on inadequate data, are of a preliminary character. However, certain interesting regularities are discernible.

MAIN MINERALOGICAL FEATURES OF THE UCHALA ORE DEPOSIT

The Uchala ore is a typical example of the copper pyrite deposits, which are associated with elongated greenstone zones in the central and southern Urals. The ore body, a thick pyrite deposit, is located among Middle Paleozoic volcanic-sedimentary meta-schistose rocks, at the contact of albitophyres and diabase-spilite effusives. The pyrite body, especially its lower side, is surrounded by an aureole varying in thickness, of sulfide inclusions and of small sub-parallel lenses and veinlets. Zavaritskii and others [1, 2] regard such aureoles as the results of metamorphic processes with redeposition and partial leaching of ore material into the enclosing rock. The latest data [4], including our own suggest a formation of ore incrustations simultaneous with the massive pyrite ores. This is confirmed by the lack of deformation in the inclusions which are represented in part by colloform segregations, also by the similarity in composition to that of the adjacent ore bodies.

The structure of the pyrite deposit is not uniform. The matrix is composed of very fine to fine-grained pyrite, accounting for 70-90% of the ore body. In it there are small "islands" of cryptocrystalline pyrite, locally containing colloform relicts. Under the microscope this pyrite shows reticulate development of fine-grained pyrite, apparently a recrystallization product of the original variety.

Some of the aggregates are nearly pure pyrite; others carry various amounts of chalcopyrite and sphalerite. Two types of occurrence predominate for these two minerals: 1) A few form fine to very fine-grained segregations within the original pyrite. The presence of chalcopyrite, and more rarely of sphalerite, in pyrite globules suggests their paragenetic relationship to the main body of pyrite. 2) The sizeable accumulations of sphalerite, and more rarely of chalcopyrite, are definitely associated with broad zones of intensified fracturing and brecciation in the pyrite ore, with these minerals concentrated in the breccia cement and in fractures. Some investigators [1, 2] explain concentration of these minerals in the cement as a phenomenon of metamorphic segregation, whereas some others [4] take them to be the result of crushing of the pyrite and of subsequent deposition of copper and zinc sulfides.

One of the authors of this paper noted that the phenomenon of ore crushing, with the formation of sphalerite-enriched breccia, was superimposed upon an earlier deformation. This one was observed in some very peculiar breccias containing large rounded fragments of fine-grained pyrite with hardly any sphalerite or chalcopyrite. Locally the rounded fragments were broken into angular chips whose cement and fractures contained segregations of sphalerite, leached ore, and locally, chalcopyrite and colloform pyrite. Thus a later deposition of these minerals is suggested, following a twice-recurring crushing of pyrite ores.

As shown on mineralogical maps, areas of chalcopyrite and sphalerite enrichment generally coincide. The affinity of these minerals is suggested by their association in intergrowths. Considering the conditions of their concentration, this definite association of sphalerite, leached ores, and a portion of chalcopyrite and pyrite can hardly be explained by metamorphic segregation.

In conclusion, emphasis should be put on the telling effect of recrystallization of pyrite in situ, and on the multiple crushing of ore material. The latter may have undergone regrouping, in the process of deformation and subsequent action caused by introduction of new solutions, but the extent appears to be comparatively limited.

STUDY METHOD AND PROCEDURE

Enough data have been accumulated to regard the sulfur isotope analysis, in conjunction with other methods, as a reliable tool in the solution of a number of geological problems, and particularly in the study of ore substance.

Previous investigations [5, 6] have shown that the isotope composition of sulfur in natural objects, under crustal conditions, is essentially variable. This variability is caused by fractionation of sulfur isotopes in the course of geologic and biologic processes. Variations in the ratio of isotopes S^{32} and S^{34} may be as large as 9%.

Vinogradov et al. [7] and Kulp et al. [8] have found that the sulfur in sulfide minerals from the same ore site has virtually the same isotopic composition, with no difference in mineral form or crystalline structure, possibly due to temperature and speed of precipitation, at least up to ±0.2%. Minerals from the same ore site but of different origin show considerable scattering of sulfur isotopes [Vinogradov et al. 7].

Jensen [9] also has found variations (up to 4%) in the isotopic content of sulfur in sulfides within a single ore site. He associates these variations with different times of formation ascribing variations of the order of tenths of a per cent either to the difference in the sources of sulfur or to a sizeable fractionation of sulfur isotopes in the separation and movement of the carrier solutions.

It has been shown theoretically [10] that the most effective separation of sulfur isotopes is observed in oxidation-reduction processes, as described by reaction $H_2S^{34} + S^{32}O_4^{2-} \rightleftharpoons H_2S^{32} + S^{34}O_4^{2-}$ (the equilibrium constant for this reaction is 1.074, at 25°C).

It has been found experimentally that in partial oxidation of H_2S to elemental S, fractionation of isotopes takes place, as a result of which S^{34} changes chiefly to a more oxidized form, thus enriching the H_2S by isotope S^{32}. In partial chemical and bacterial reduction of dissolved sulfate to H_2S, the latter is enriched in the light isotope, whereas the sulfate is enriched in the heavy isotope. The speed of fractionation depends on the relative quantities of the original sulfate and the resulting sulfide, and on the temperature and speed of the process [11]. Processes other than oxidation-reduction, which lead to isotope fractionation of S in natural objects are possible, but they are not well known. Thus it appears that the isotopic analysis of S, together with mineralogical data, may be used as a criterion of the differences and evolution of the sources of sulfur-bearing solutions, as well as of certain specific features of the mineral-forming reactions.

Some 44 specimens of sulfides and sulfates from this ore deposit have been analyzed in the course of this study. The results are given in the table. The processing of the specimens and the determination of the sulfur isotope content was carried out by the method described by Vinogradov et al. [12]. Sulfur from the Sikhote-Alin meteorite was taken as a standard, with the isotope ratio S^{32}/S^{34} = 22.20. The sulfur isotope content was measured with a MS-2 mass-spectrometer, with a measurement error of ±0.01-0.02%.

Since the cement of brecciated ores was a fine-grained aggregate of pyrite, sphalerite and barite, these minerals were chemically separated. A quantity of finely-pulverized cement was processed in a flow of N diluted by HCl. In this process, sphalerite was decomposed and the escaping H_2S absorbed by lead acetate. The lead sulfide thus obtained was analyzed for the sulfur isotope content of sphalerite. The quantity remaining after the extraction of sphalerite was then processed with bromine and nitric acid, to oxidize the sulfur of pyrite to sulfate. The barite in the residue was filtered out and analyzed for the sulfur isotope content. The pyrite sulfur was precipitated out of the filtrate with barium chloride. Barium sulfate was changed to PbS, which was used in the determination of the isotope composition of the pyrite sulfur.

An average sample of cement was taken from four specimens. The sample was processed with bromine and nitric acid, to oxidize the sulfide to sulfate, which was then precipitated with barium chloride and filtered out, together with the barite of the cement. Barium sulfate thus obtained was changed to PbS which was used in the determination of the total isotope content of the sulfur contained in the cement.

EVALUATION OF RESULTS

The minerals studied were varieties of pyrite, chalcopyrite, sphalerite, and barite, occurring as associated minerals in the Uchalin ore body. A correlation of the data reveals an essentially variable sulfur isotope content in the ore minerals of that locality. Deviations from the standard are generally 0-0.83% for sulfides, and 1.1-3.25% for barites.

Isotope Composition of Sulfur from Sulfides and Sulfates of the Uchala Formation

No. of sample	Description of sample	Deviation from Standard	S^{32}/S^{34}
	Massive and disseminated pyritic ores		
1.	Cryptocrystalline pyrite from massive pyritic ores	-0.03	22.194
2.	Cryptocrystalline pyrite from massive pyritic ores associated with pyrite (3)	+0.03	22.206
3.	Coarse-grained pyrite from massive pyritic ores, associated with pyrite (2)	0	22.20
4.	Coarse-grained pyrite from massive pyritic ores	0	22.20
5.	Coarse-grained pyrite, disseminated in quartz-sericite rocks	0	22.20
6.	Coarse-grained pyrite, disseminated in quartz-sericite rocks	+0.03	22.206
7.	Chalcopyrite, widely disseminated in massive pyritic ores, associated with sphalerite (9) and barite (11)	+0.2	22.244
8.	Chalcopyrite, disseminated in massive pyritic ores, associated with sphalerite (10) and barite (12)	+0.38	22.284
9.	Sphalerite, widely disseminated in massive pyritic ores, associated with chalcopyrite (7) and barite (11)	+0.1	22.222
10.	Sphalerite, disseminated in massive pyritic ores, associated with chalcopyrite (8) and barite (12)	+0.36	22.280
11.	Barite, widely disseminated in massive pyritic ores, associated with chalcopyrite (7) and sphalerite (9)	-1.177	21.807
12.	Barite, disseminated in massive pyritic ores, associated with chalcopyrite (8) and sphalerite (10)	-1.45	21.878
	Breccia ores (sphalerite-chalcopyrite association)		
13.	Coarse-grained pyrite from breccia fragment	-0.04	22.191
14.	Coarse-grained pyrite from breccia fragment	-0.06	22.187
15.	Coarse-grained pyrite from breccia fragment	-0.06	22.187
16.	Coarse-grained pyrite (reprecipitated?) from center of breccia fragment	-0.18	22.160
17.	Fine-grained pyrite, a fringe after coarse-grained pyrite (16)	-0.1	22.178
18.	Coarse-grained pyrite (reprecipitated) from breccia fragment, associated with chalcopyrite (29) and barite (30)	-0.43	22.105
19.	Pyrite from breccia cement	0	22.20
20.	Pyrite from breccia cement	-0.02	22.220
21.	Pyrite from breccia cement, associated with sphalerite (26) and barite (32)	-0.21	22.153
22.	Pyrite from breccia cement, associated with sphalerite (27) and barite (33)	-0.15	22.167
23.	Pyrite from breccia cement, associated with sphalerite (28) and barite (34)	-0.28	22.138
24.	Sphalerite from breccia cement	-0.13	22.174
25.	Sphalerite from breccia cement, associated with barite (36)	-0.83	22.016

Isotope Composition of Sulfur from Sulfides and Sulfates of the Uchala Formation (Continued)

No. of sample	Description of sample	Deviation from Standard	S^{32}/S^{3}
26.	Sphalerite from breccia cement, pyrite (21) and barite (32)	-0.2	22.15
27.	Sphalerite from breccia cement, associated with pyrite (22) and barite (33)	-0.3	22.13
28.	Sphalerite from breccia cement, associated with pyrite (23) and barite (34)	-0.26	22.14
29.	Chalcopyrite from breccia fragment, associated with pyrite (18) and barite (30)	-0.24	22.14
30.	Barite from breccia fragment, associated with pyrite (18) and barite (29)	-2.01	21.75
31.	Barite from breccia fragment	-2.35	21.67
32.	Barite from breccia cement, associated with sphalerite (26) and pyrite (21)	-1.1	21.95
33.	Barite from breccia cement, associated with sphalerite (27) and pyrite (22)	-1.25	21.92
34.	Barite from breccia cement, associated with sphalerite (28) and pyrite (23)	-1.95	21.76
35.	Barite from breccia cement	-1.25	21.92
36.	Barite from breccia cement, associated with sphalerite (25)	-3.25	21.47
37.	Average sample of breccia cement, including pyrite (21, sphalerite (26), and barite (32)	-0.45	22.10
38.	Average sample of breccia cement, including pyrite (23), sphalerite (28) and barite (34)	-0.47	22.09
39.	Average sample of breccia cement, including pyrite (22), sphalerite (27), and barite (33)	-0.33	22.12
40.	Chalcopyrite from massive copper ores, associated with pyrite (42)	-0.5	22.08
41.	Chalchopyrite from disseminated copper ore	-0.57	22.07
42.	Pyrite from massive copper ore, associated with chalcopyrite (40)	-0.25	22.14
43.	Fine-grained pyrite, from vein in breccia cement,	-0.13	22.17
44.	Fine-grained pyrite, from vein in breccia cement associated with sphalerite (28), pyrite (23) and barite (34)	-0.4	22.11

Comments: - sign means S^{34} enrichment
+ sign means S^{32} enrichment
The sample numbers are given in the margin.

Fine-grained pyrite varieties of massive pyrite ores, associated with its earlier generations, revealed negligible deviations from the standard, on the order of ±0.03%, with a comparative stability for different segments of the ore deposit (specimens 1, 2).

Significantly, coarse-grained pyrite (specimens 3, 4), developed on the fine-grained does not differ from it in isotope composition, wherever evidence of later brecciation is lacking. The deviations from the standard in it do not exceed 0.03%, and commonly are altogether lacking. Deviations of the order of ± 0.03% may be due to slight temperature differences during primary precipitation of sulfides; in any event, they lie at the boundary of the margin of error.

This corroborates the concept that the coarse-grained variety of pyrite in massive ores is a product of recrystallization of earlier, fine-grained pyrite, with the similarity in the isotopic content of their sulfur testifying to the absence of addition or subtraction.

Pyrites from inclusions in the surrounding schists, taken from different localities (specimens 5, 6), had a consistent isotope content, not different from that in sulfur from earlier pyrites of the massive ores. This similarity in sulfur isotope content contradicts the idea of these inclusions having been formed by solution and reprecipitation of the substance of primary ores. Had this occurred, a change in the isotopic content in sulfur of the reprecipitated substance could be observed. On the other hand, this similarity in composition is easily explained by a synchronous deposition of pyrite in ore bodies and in fractures of the enclosing rocks.

A determination of the sulfur isotope content in sphalerites and chalcopyrites (specimens 7, 8, 9, 10), scattered in isolated incrustations throughout massive pyrite ores, shows a substantial enrichment of these minerals by the S^{32} isotope. Deviations from the standard range from + 0.1% to + 0.38%. The associated barites (specimens 11, 12) show a high isotope S^{34} content, which is in accordance with the idea of heavy isotope accumulation in more oxidized forms. Judging from the results of the isotopic analysis, it can be assumed that, in this instance, the "solution" out of which the massive pyrite ores were formed had contained, beside iron, small amounts of Cu, Zn, and Ba. Subsequent to the crystallization and combination of the bulk of the sulfide sulfur, the oxidation-reduction potential of the residual solution apparently changed, and a portion of sulfur was oxidized to SO_4^{2-} ion which combined with Ba and was precipitated as poorly-soluble barite. The unoxidized sulfur, on the other hand, was enriched by the light S^{32} isotope and formed sphalerite and chalcopyrite. This explanation is presented here as a tentative one.

Very significant are the results of the isotopic analysis of sulfur from the sphalerite-chalcopyrite combination which is associated with the brecciated zones of pyrite ores. Their isotope content, in contrast to that of sulfides of the massive pyrite ores, shows a regular enrichment by the heavy isotope S^{34}. Deviations from the standard are 0-0.4%, for pyrites; for sphalerite of massive ores, enrichment by the heavy S^{34} isotope is noted to the extent of 0.2-0.3%, as compared with the standard.

The isolated inclusions of sphalerite, chalcopyrite, and leached ores should not be regarded as a result of plastic deformation and subsequent recrystallization since, in that case, they would not have acquired the distinctive differences in sulfur isotope content, as compared with the sulfur of earlier sulfide associations. Either a full reprecipitation of the substance of these minerals or their separation out of some special portion of solutions must be assumed; the latter appears to be more probable. The substantial difference in sulfur isotope content for these sulfides, and their enrichment by the heavy isotope, suggest a source of solutions different from those which produced the earlier massive pyrite ore minerals, or else a fractioning of the isotopes in the process of evolution of a single source, with accumulation of heavier S isotopes at later stages. A theoretical substantiation of the idea of the sulfur isotope fractioning, in such a process, is lacking. However, the qualitative difference in the sulfur isotope content in pyrite ores and in copper-zinc ores definitely shows the difference in mineralizing solutions at various stages of ore deposition. The sizeable variations in the sulfur isotope content of sulfides and sulfates from the sphalerite-chalcopyrite association suggest a complex process of formation for these ores.

A correlation of the results of sulfur isotope analysis and the mineralogical data leads to the following assumptions. In superimposing, after brecciation, of Cu and Zn associations upon earlier pyrite ores, some complex metasomatic phenomena evidently took place, as a result of which the material of brecciated ores was partly replaced by new mineral segregations, while the cement preserved the incompletely decomposed relicts of earlier segregations. Variations in the sulfur isotope content of pyrites and in the mineral components of the sphalerite-chalcopyrite combination corroborate this assumption. Sulfur from later Cu-Zn solutions could partially mix with the sulfur of crushed and corroded pyrite grains, in some cases (specimens 13, 14, 15, 19, 20), or form an average isotope composition in recrystallization and reprecipitation of pyrite, depending on the amount of original pyrite and solution, in the others (specimens 16, 17, 18, 21, 22, 23).

As shown by the isotopic analysis, Cu-Zn solutions as a whole were substantially enriched by isotope S^{34}. The isotope content for the average sample of brecciated ore (specimens 37, 38, 39), approximately corresponding to the original isotopic composition of the solution which has deposited the minerals of the sphalerite-chalcopyrite combination, shows considerable enrichment (up to 0.5%) of that solution by S^{34} isotope. The average sample might have shown a lower enrichment by the heavy isotope because of contamination of the sulfur of that solution by the lighter sulfur from the relict pyrite.

Sphalerite in the cement of brecciated ores differs in its isotope composition from the average sample, and shows considerable variations in the content of isotopes S^{32} and S^{34} (specimens 24, 25, 26, 27, 28). This can be explained, on the one hand, by contamination of sulfur from the sphalerite by lighter sulfur from pyrite which had been previously replaced; or, on the other hand, by fractioning of sulfur isotopes in solution, in the oxidation-reduction processes, as suggested by the presence of barite in the ore.

As to the chalcopyrite in massive (specimen 40) and disseminated (specimen 41) copper ores, it obviously had the same source of sulfur as for the sulfides (sphalerite) in the cement, since its sulfur isotope content is close to that of the average sample of brecciated ore cement. It should be noted that no barite was found in the analyzed specimens of chalcopyrite, which suggests either the absence or poor development of oxidation-reduction processes in the formation of that mineral; accordingly, its isotopic composition best corresponds to that of the original solution. In some instances, the comparatively low heavy isotope content in chalcopyrite (specimen 29) may be explained by its contamination with lighter sulfur of the pyrite metasomatically replaced by it (specimen 8).

All of the analyzed specimens of brecciated ore have been found to contain barite as well as sphalerite in their cement. Variations in the sulfur isotope content of the barites show that these minerals could not have originated from the same sulfate solution, since in that case they would have had the same sulfur isotope content. Their origin is due rather to partial oxidation of the sulfide solution, with different speeds of oxidation for different localities.

SUMMARY

1) Sulfides of the Uchala copper pyrite ores differ substantially in the sulfur isotope content, although these differences are not conditioned by their mineral aspect, nor by local conditions of mineralization.

2) Variations in the sulfur isotope content for different sulfide complexes, along with the mineralogical data, suggest the association of these sulfides with different stages of ore formation.

The similarity in the sulfur isotope content of pyrite—the main component of the ore body—and that disseminated in the enclosing rock, suggests a common sulfur source, i.e., a common source of mineral-forming solutions, and consequently their contemporaneous origin. The sulfur isotope content for sulfides of massive and disseminated pyrite ores is identical with that for volcanic sulfur.

3) Oxidation-reduction processes held considerable sway during the last Cu-Zn stage of ore formation, leading to fractionation of S isotopes in the process of mineral formation.

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EFFECT OF MINERAL STRUCTURE ON THE ISOMORPHOUS REPLACEMENTS IN SILICATES OF EFFUSIVE ROCKS

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Abstract

The influence of the structure of crystalline silicate lattices upon the distribution of rare elements in the minerals of igneous rocks is shown in a number of examples. The predominant rubidium concentration in biotite and the proportional distribution of barium and lead among the biotite and the potassium feldspar of the rocks is established and brought into connection with the peculiarities of the structural position of potassium and aluminium in the lattices of these minerals.

In the case of lithium and germanium, the assumption is expressed that the influence of the structures of minerals upon isomorphous replacements in silicates affects the geochemical history of these elements in the magmatic process.

In the analysis of isomorphous phenomena in silicates, most attention is given to such crystallochemical properties of elements as their ionic radius, electronegativity, or the ionization potential. It is quite clear that these individual properties of elements determine in many instances the possibility of their entry into various crystal structures. However, of no less importance are the structural features of the host minerals that contain them.

The general significance of crystalline features was noted by the late V. M. Goldschmidt through his formulation of the conditions for formation of mixed crystals. Foremost among the main conditions for their formation, he puts the similarity in the chemical structure of the participants and, then, the similarity in their crystal-lattice type. Now, however, such general formulation of the conditions for formation of mixed crystals should be broadened and rendered more specific.

First of all, it should be noted that the features of crystal structures will become extremely important in the determination of the limits of isomorphous association. It is obvious that only a few pairs of elements are marked by very close crystallochemical properties. Other elements are more or less different in such properties.

It is natural that elements with sharply different crystallochemical properties will not enter into isomorphous associations. Such association, however, is possible for elements with smaller crystallochemical differences. The limits of isomorphism will be determined, not by the degree of the crystallochemical differences in the participating elements alone, but by other factors as well. Among the latter, an important part is played by the properties of the crystal structures housing these replacements.

In considering the effect on isomorphous replacements of the structural features of the crystal lattices of minerals, the first important factor is the mineral composition. Specifically, it may be stated for rock-forming silicates that the more components in a mineral, the better is the chance for isomorphous replacement. It should be added that the peculiarities of silicate components will be especially revealing in heterovalent isomorphous replacements. Very significant in th respect are the data on isomorphous admixtures in olivines and associated pyroxenes, as obtained by Wager and Mitchell [1] in their study of the geochemistry of rare elements from the Skaergaard intrusion (eastern Greenland).

According to their data, the isomorphous admixture in olivines is represented chiefly by those elements which have the same charge, such as Mg^{2+} and Fe^{2+}, and similar ionic radii (Ni, Co, Cu^{2+}). Elements with ionic radii close to those for Mg and Fe, but carrying different charges, are present to a considerably smaller extent.

In contrast to the olivines, the associated pyroxenes are marked by a considerably larger group of admixtures. The presence in the octahedral coordination of such elements as Al and Fe^{3+} determines the appearance of sizable amounts of Cr and V. An admixture of Sc and Zr is characteristic for all pyroxenes analyzed by these authors.

The data of Wager and Mitchell, as well as of other authors, have definitely shown more admixed elements in pyroxenes, which are mor complex in their compositions, than in orthosilicates. Moreover, the latter are characterized chiefly by isovalent isomorphous replacements which require no compensation. With pyroxenes, on the other hand, heterovalent replacements are developed to a somewhat greater extent, as well as the isovalent.

In considering the effect of the lattice structure of minerals on the isomorphous replacements in rock-forming silicates, the significance of coordination number is paramount. Even diagrammatic geometric constructions demonstrate clearly that a raised coordination number leads to compaction of the structure, that is, to a more economical use of space.

In evaluating the significance of coordination number for deciphering the isomorphism phenomena, one of the most important problems of the crystallochemistry of silicates is the possible limit of aluminu entry into the silicon position. As well known, two lines of mineral development are observed in the crystallization of silicate melts. This recently was promulgated by Belov [2]. A study of the crystallization process of silicate melts shows the leucocratic rock components (feldspar, quartz), characterized by structures considerably deviating from the most compact, correspond to the maximum polyme ization of Si-O tetrahedrons, whereas they are distinguished by the maximum ratios of aluminum in quadruple coordination to silicon in the beginning of the crystallization of the melt (basic feldspars). Further crystallization proceeds in the direction of a decrease in the tetrahedral aluminum content in the leucocratic component (alkaline feldspars - quartz).

A somewhat different picture is observed for the crystallization of the melanocratic rocks (pyroxenes, amphiboles, micas), as characterized by structures with more compact packing. The initial stages of crystallization of the melanocratic components are marked by a low degree of polymerization of Si-O tetrahedrons (orthosilicates and pyroxenes) with a low ratio of Al in quadruple coordination to Si. In the process of crystallization, not only a strengthening in polymerization of Si-O tetrahedrons in the melanocratic components is observed, but an increase of Al proportion in these tetrahedrons as well. Biotite is the terminal member of this series of the maximum polymerization of the tetrahedrons and of the maximum amount of tetrahedral Al. However, only a quarter of the Si-O tetrahedrons are replaced by the Al-O tetrahedrons in this terminal member of the melanocratic series, whereas, in the initial members of the leucocratic series (basic plagioclases), a half of these tetrahedrons are so replaced.

Such a limited Si-Al exchange in biotites, as compared with feldspars, results from significant differences in the structures of these two mineral groups.

Micas (biotite) have structures corresponding to a somewhat modified close packing, whereas the structures of feldspars cannot be reduced to any order of packing. A compact packing in mica sheets makes possible the replacement of a large number of Si-tetrahedrons by Al-tetrahedrons. This may be due to the fact that the ratio of Al^{3+} to O^{2-} ion radii is the upper limit for four-fold coordination. The formation of such Al-tetrahedrons is probably accompanied by some pushing apart of anions and by a consequent departure from the closest packing.

This problem is closely related to the isomorphic capacity of leucocratic and melanocratic components of rocks for certain elements. Specifically, the isomorphic capacity of biotite and K-feldspar with relation to Pb, Ba, Rb, and Tl is of great significance. These four elements are crystallochemically close to K, but in different degrees.

At the same time, the distribution of these elements in K-feldspars and biotites has certain peculiarities not explicable by the individual crystallochemical properties of mutually replacing elements. Their distribution is connected rather with the structural features of these two minerals and more specifically with the structural situation of K and Al.

The amounts of Rb, Ba, and Pb in biotites and feldspars are best expressed as atomic ratios of these elements to those of K through the use of so-called concentration coefficients, which show the concentration of a given rare element for a particular mineral in comparison with its concentration in nature. Analyses of three granitoids from Scotland (made by Nockolds and Mitchell[3]), and of two granitoids from the Susamyr batholith (made by the author) served as initial data The K-content in K-feldspars from central Tien-Shan granitoids was computed from the average content of this element in a particular mineral. All other figures were obtained analytically.

The data of Table 1 demonstrate that Rb tends to concentrate in biotite in a definite manner. As is seen from the table, there are 6 to 7 times more Rb atoms than the K-atoms to the same amount of K-feldspar. The concentration coefficients demonstrate that only biotite may be taken as a Rb-concentrating mineral, since for K-feldspars these coefficients are < 1.

Thus, it can be said of the isomorphic possibilities for Rb in biotite and K-feldspar that, because of more freedom in K, the larger Rb ion enters biotite with more ease than it enters K-feldspar. This is much more so because the $r_{Rb^+}:r_{O^{2-}}$ ratio is somewhat > 1, and the 12-fold coordination, associated with K in biotite, is more convenient for such a large ion as Rb^+.

The ion radius of Ba^{2+} is very close to that of Rb (Ba^{2+}, 1.43 Å; Rb 1.49 Å). Likewise, the ratio $r_{Ba^{2+}}/r_{O^{2-}} > 1$ would seem to call for the 12-fold coordination for Ba and for its priority in the entry into biotite. However, the data of Table 1 show no such preferential accumulation of Ba in biotites. Furthermore, the concentration coefficient for Ba in K-feldspar is < 1; it is somewhat larger than in the corresponding biotites. This proves that no K-minerals may be regarded as a Ba concentrator. On the other hand, this suggests that not all of the Ba in rock crystallochemically accompanies K. The balance of Ba from the monomineral fractions of the Morven-Stronshen tonalite shows that about 40% of Ba in rock is connected with plagioclase. Thus, the distribution of Ba and Rb is essentially different. The reason appears to be that, in the isomorphous replacement of K by Ba, a replacement of another pair of elements is needed to reestablish the electrostatic balance of the lattice. In K-feldspar, such a replacement proceeds according to formula: $Ba^{2+}Al^{3+} \rightarrow K^{+}Si^{4+}$.

In K-feldspars, in analogy with plagioclases, this replacement does take place, despite the fact that it is not advantageous, energy-wise. It also takes place in biotites, but here it appears to be even more restricted. The restrictions are due not only to the negative energy-wis effect of such isomorphic reaction, but also to the fact that the compe sating replacement of Si atoms by Al is difficult in those minerals. A a result, the favorable factor of the high K coordination in biotite is neutralized, so to speak, by these restricting factors, and Ba does not accumulate in biotite as compared with K-feldspars.

As seen from Table 1, a similar situation is observed for Pb; in this case, its concentration coefficient is virtually the same for both biotite and K-feldspar. At the same time, the data show that only a portion of Pb crystallochemically accompanies the K in rocks. The io radius of Pb^{2+} is nearly the same as that of K^+ (Pb^{2+}, 1.32 Å; K^+, 1.33 Å). As far as the theory of coordination is concerned, Pb, next to

Rb, should be concentrated in biotites. This, however, has not been observed. Such a selectivity in the accumulation of Pb in biotites appears to be due to two causes. On one hand, there is the same restricting factor as for Ba: the difficulty of the replacement of Si^{4+} by Al^{3+} in biotites; on the other, the type of chemical association with oxygen differs for K and Pb.

Because of its high electronegativity, Pb associations with oxygen should have a sizable proportion of the covalent component. This, however, always leads to the tendency of the element toward a lower coordination, thus giving identical isomorphic possibilities for Pb in both K-feldspars and biotites.

All of the studied instances of the isomorphous entry of Rb, Ba, and Pb into biotite and K-feldspars demonstrate the importance of the crystalline structure of substances as a factor of isomorphism. In some instances, the features of the isomorphous entry of a rare element into minerals, as determined by the structure of those minerals, are of no small importance in the geochemical history. A case in point is Li and Ge.

A study of Li distribution throughout effusive rocks reveals an apparent contradiction in the chemical history of Li during the magmatic stage. Li is crystallochemically bound to Mg,

Table 1. Relationship of Rb, Ba and Pb to Potassium in Biotites and Potassium Feldspars of Several Granitoids

	Morven-Stronshen tonalite (Scotland)			Morven-Stronshen granite (Scotland)			Garaball Hill granite (Scotland)			Dzhumgol Range granite (Central Tien-Shan)			Dzhumgol R. leucocratic granite (Cent. Tien-Shan)		
	rock	biotite	potassium feldspar	rock	biotite	potassium feldspar	rock	biotite	potassium feldspar	rock	biotite	potassium feldspar	rock	biotite	potassium feldspar
$Rb_{at} \cdot 10\,000/K_{at}$	28	62	2	54	156	23	—	—	—	19	68	16	20	69	11
Coeff. of conc. Rb $\left(\frac{Rb_{at}/K_{at}min.}{Rb_{at}/K_{at}rock}\right)$	—	2.21	0.07	—	2.89	0.42	—	—	—	—	3.59	0.84	—	3.45	0.55
$Ba_{at} \cdot 10\,000/K_{at}$	180	97	122	—	—	—	200	122	130	—	—	—	—	—	—
Coeff. of conc. Ba $\left(\frac{Ba_{at}/K_{at}min.}{Ba_{at}/K_{at}rock}\right)$	—	0.54	0.68	—	—	—	—	0.61	0.65	—	—	—	—	—	—
$Pb_{at} \cdot 10\,000/K_{at}$	—	—	—	—	—	—	—	—	—	1.0	0.7	0.7	1.4	0.7	0.6
Coeff. of conc. Pb $\left(\frac{Pb_{at}/K_{at}min.}{Pb_{at}/K_{at}rock}\right)$	—	—	—	—	—	—	—	—	—	—	0.7	0.7	—	0.50	0.43

and escapes into ferro-magnesium silicates as an isomorphous admixture during the crystallization of rocks. Its geochemical history in the process of magmatic differentiation contradicts that of Mg: in the differentiation series, Li concentration increases with a decrease in Mg content. This is because Li does not replace Mg with the same ease in different ferro-magnesium silicates. This is very graphically illustrated by the data of Table 2.

This table shows that pyroxenes and hornblendes from these rocks hardly may be regarded as Li concentrators. Despite the fact that Mg content in hornblendes is nearly the same as for biotites, no Li concentration in them has been observed; and the melts residual to the crystallization of these ferro-magnesian minerals will be enriched by Li. This is indicated by the ratio of the atomic amounts of Li and Mg, which is on the average nearly ten times greater in the rocks than in the corresponding hornblendes. In contrast with hornblendes, the biotites from these rocks nearly always are concentrators of Li. The ratio of the atomic amounts of Li and Mg in these minerals exceeds that for the corresponding rocks by nearly the factor of two on the average.

Thus, the western Scotland rocks show biotite to be the main

Table 2. Relationship of Lithium and Magnesium Concentrations in Ferromagnesian Silicates of Several Rocks
(Conversion from data by Nokkolds and Mitchell [3])

Rock	$Li_{at} \cdot 1000/Mg_{at}$				Coeff. of conc. of Li*	
	In rock	In pyroxene	In hornblende	In biotite	In pyroxenes and hornblendes	In biotite
Garaball-Hill pyroxene-mica diorite	1.3	0.05	–	2.7	0.04	3.1
Garaball-Hill "xenolith" diorite	3.7	–	0.45	11.1	0.12	3.0
Garaball-Hill medium-grained granodiorite	6.3	–	0.7	10.4	0.11	1.7
Morven-Stronshen tonalite	10.3	–	1.3	32.3	0.12	3.1
Morven-Stronshen granodiorite	6.6	–	0.4	14.6	0.06	2.2
Ben-Nevich granodiorite	9.9	–	1.0	20.0	0.11	2.2

*The concentration coefficient is defined by the ratio $\frac{Li_{at}/Mg_{at}\ \text{mineral}}{Li_{at}/Mg_{at}\ \text{rock}}$

concentrator and carrier of Li. Preferential concentration of Li in biotites, as compared with other ferro-magnesian silicates, is also noted by other authors [1, 4].

The reason for low concentrations of Li in orthosilicates is quite understandable if we are to consider that heterovalent isomorphous replacements in them are hampered by difficulties in the compensation of their charges.

Pyroxene structures are more favorable for the isomorphous entry of Li. As much is indicated by the wide distribution of Li-pyroxene (spodumene, $LiAl(Si_2O_6)$) in nature; it is generally confined to pegmatites. A scheme of the isomorphous replacement of Mg by Li may be represented as $2Mg^{2+} \leftarrow Li^{+}Al^{3+}$. Calculations show that such a scheme is advantageous, energy-wise, as it leads to the formation of sufficiently stable structures. In this connection, it appears that the reasons for a lowered Li content in pyroxenes (as compared with biotites) should be looked for elsewhere, and primarily in the chemical bonds within minerals. Ramberg [5] noted recently that the ionic character of the bonds between oxygen and cations, in silicates, increases with the degree of polymerization of Si-O tetrahedrons. Thus micas form stronger acid radicals than the pyroxenes. At the same time, a comparison of the electronegativity of Li and Mg (1.0 and 1.2 respectively) shows Li to be the stronger cation in this respect. Considering all this, and other conditions being equal, it may be assumed that Li would tend to unite with the stronger mica radicals rather than with those of pyroxenes.

A somewhat different situation may be assumed for the isomorphous replacement in hornblendes: $Mg^{2+}Na^{+} \leftarrow Li^{+}Ca^{2+}$. Such a scheme is not advantageous, energy-wise; therefore, the low Li contents in these minerals may be explained not only by the smaller degree of polymerization of the Si-O tetrahedrons in amphiboles, as compared with micas, but also by the energy effects of such replacement.

Finally, in evaluating the factors of the preferential entry of Li into the biotite structure, it should be noted, as a very important feature of its concentration in this mineral, that the precipitation of biotite takes place chiefly in the final stages of rock crystallization when the residual solutions are substantially enriched by Li.

Thus, the data cited show that in the minerals of effusive rocks, the crystallochemical affinity of Li and Mg is not manifested to the same degree.

In orthosilicates, pyroxenes, and amphiboles, the crystallochemical bonds of Li and Mg are complicated by a number of structural factors hampering the isomorphous entry of Li into these minerals. Biotite is the only mineral in effusive rocks where the crystallochemical affinity of Li and Mg is manifested in full. In connection with the distribution of Li throughout the rocks, Li probably will be accumulated in the process of differentiation of magmatic foci in those differentiates with the maximum of their Mg atoms bound in biotite (granodiorites and biotite granites). A decreased Li content may be expected in the leucocratic varieties of granitoids, especially in aplite dikes. This feature of Li distribution in minerals clarifies to a certain extent the above-mentioned alleged contradiction in the geochemical history of Li in its magmatic stage.

In considering the geochemical features of germanium in extrusive rocks, most students note an adequate crystallochemical and geochemical relation between Ge and Si. This is due primarily to the crystallochemical properties of these two elements. In its place in Mendeleyev periodic system (similar to that of Si) Ge is also close to it in its ion radius (Si^{4+}, 0.39 Å; Ge^{4+}, 0.44 Å), in its value of electro-negativity (Si^{4+}, 1.8; Ge^{4+}, 1.7), and ionization potential.

However, despite such similarity in the crystallochemical properties, Ge does not isomorphously enter the silicates with the same ease Specifically, Harris [6] demonstrated recently that the Ge content in orthosilicates and pyroxenes usually is 2 to 8 times as great as in the associated feldspars. Obviously, this is connected with the structural features of the minerals, and with the fact that Ge is not noted for its entry into polyacids similar to the polysilicates. This is why it enters the lattices of those silicate compounds with the least polymerization of Si-O tetrahedrons. The observed preferential concentration of Ge in orthosilicates and pyroxenes appears to be reflected in the character of distribution of this rare element throughout the main effusive types of rocks. Of course, if Ge entered all silicate minerals with the same ease, the critical factor on the magmatic stage of its geochemical history would have been the behavior of Si in the process of differentiation. This, in turn, would mean the same degree of Ge enrichment in acid rocks as it is for Si. However, the effect of the preferential concentration of Ge by orthosilicates and pyroxenes distorts this picture, as it leads to the fixation of a somewhat larger portion of Ge atoms in the differentiates enriched by Si.

As a result, this rare element is more or less evenly distributed in the main types of extrusive rocks.

The instances cited demonstrate that the structures of minerals are one of the paramount factors regulating the distribution of rare elements in the processes of rock crystallization. Moreover, in a number of instances the structural factor predetermines to a considerable extent the entire geochemical history of the element during the magmatic stage. Therefore in analyzing the conditions of the distribution of rare elements isomorphously entering the effusives and their component minerals, the structural features of the latter should be kept in mind. This is especially important in establishing the isomorphic potentiality of a given rare element and in the determination of the isomorphic capacity of a mineral in regard to a specific rare element.

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THE ZIRCONIUM-HAFNIUM (CELTIUM) RATIO IN THE LOVOZERO MASSIF ROCKS

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Abstract

The zirconium and hafnium content in rocks of the Lovozero massif (Kola Peninsula) varies in wide ranges from 0.071 to 2.31% ZrO_2 and from 0.015 to 0.057% HfO_2, whereas the ZrO_2/HfO_2 ratio varies insignificantly from 32 to 54 The zirconium content in the miascite rocks of the massif (0.167% ZrO_2) is lo er than in the agpaitic rocks (0.290% and 1.49%). In agpaitic rocks, no direct i terdependence exists between the sodium and potassium content on one hand a the zirconium and hafnium content on the other hand. At the end of the magma process an accumulation of zirconium and hafnium occurs.

Zirconium and hafnium are chemically similar. Hafnium occurs only in Zr-containing minerals. However, the Zr/Hf ratio varies for different minerals. Up to now the attention of the students was direct chiefly to the distribution of Zr and Hf in minerals and of Zr in rocks [1, 2, 3, 4]. The literature has but a few data on Hf content in magma rocks. Two figures are usually given: that by Sahama (spectroscopic analysis of a mixture of 34 granites) and Hevesy (radiospectroscopic analysis of a mixture of 300 intrusive rocks). Besides these figures, data were published recently on the Hf content in the granitoids of the Verkhiset intrusion [5].

As is noted from numerous works on the Zr-Hf ratio in various Zr carrying rocks, this ratio is subject to considerable variation. It has been noted, for instance, that it is much smaller in Zr minerals genet cally connected with granites (about 20-50) than in minerals from nep eline syenites (usually 60-200). The results of our own studies [7] have shown that the ratio ZrO_2/HfO_2 for Zr from the Lovozero nepheline-syenite massif (Kola Peninsula) varies from 45 to 57. In view of this, and the fact that published data on Hf content in nepheline syenite are lacking, we undertook a study of this ratio in the rocks of that massif.

The Lovozero massif is an intrusion which has been formed in several stages. It is made up of the following rocks (beginning with the more ancient):

I. Coarse-grained porphyritic, poikilitic and other nepheline syenites

II. Lujavrites, foyaites, urtites

III. Eudialyte lujavrites and associated porphyritic lujavrites, tavites and poikilitic soda-feldspars

IV. Younger dike rocks (dike complex)

The main component of the massif is complex II (lujavrite-foyaite-urtite) which makes up its lower part, about 900-1000 m thick; then complex III (eudialyte lujavrites) making up the upper part, 300-400 m thick.

The following minerals in the Lovozero massif carry the most Zr:

	ZrO_2 content %		ZrO_2 content %
Zircon	65.00	Mn-zircopal	11.63
Catapleiite	31.00	Chinglusuite	2.80
Zirfesite (cyrtolite?)	30.47	Zr-halloysite	2.8 - 3.5
Titanolavenite	16.72	Lomonosovite	0.91 - 2.51
Lovozerite	16.00	Murmanite	1.40 - 2.08
Eudialyte	11.00 - 44.00		

From among these minerals, only a few are widely distributed in nature, namely eudialyte, lovozerite, lomonosovite, and murmanite. The concentration of these minerals in agpaitic rocks of the massif, which were formed in the second and third intrusive stages, is commonly so high that they are not merely secondary but also rock-making minerals (eudialyte lujavrites, porphyritic lovozeritic lujavrites, etc.). The results of our analysis of Zr and Hf in the rocks of the massifs are given in Table 1.

The radiospectroscopic method was used for the determination of Zr and Hf content in rocks, with preliminary enrichment of the sample, by the usual method [5]. Enrichment is necessary because the Hf and Zr content in rocks is below the average limit of sensitivity for this method.

The analysis was performed using a long-wave X-ray spectrograph, with a quartz crystal bent at a radius of 500 mm (plane 1120), as the analyzer. In contrast to the earlier method [1], the Zr and Hf determination in the sample was done from a single graduating graph. This was possible because the experimental conditions were so selected that dark bands LB_1-Hf and KB_1-Zr became identical at ratio Zr/Hf = 40. In this way, with four runs on the spectrograph (2 for standard and 2 for the sample), and on an appropriate scale, four points of the graduating graph are obtained, for computation.

Figure 1 presents a typical graph for analysis of total Hf and Zr, chemically separated out of rock. In those cases when the Hf-Zr content is lower, standards with a correspondingly lower content are selected.

Experience has shown that scattering of values $\Delta S = S_{1+f} - S_f$ (for the same content of the element) within each film is considerably less than for different films. Consequently, the determination error will be smaller in comparing ΔS for standards and samples, on the same film.

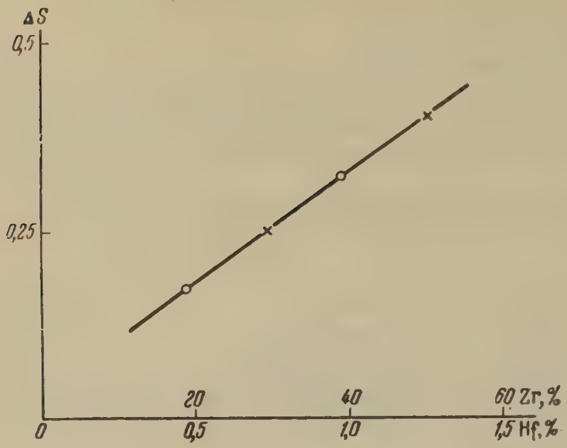

Fig. 1. Graduated graph for the determination of hafnium and zirconium content in a sample.

O—Hf, X—Zr

For better result each sample was exposed twice, i.e., on two films. The first film takes in two samples and two standards, with Zr and Hf contents approximately corresponding to those in samples. After calculation of the first film, and estimation of the amounts of the elements in the spec mens, standards are selected with the Hf-Zr content nearest t them. Average erro in determination fro two films does not e ceed ± 4%, for Hf co tent > 0.1% and Zr content > 5%. For lower contents, the error increases up to ± 12%.

Along with the radiospectroscopic determination of Hf-Zr content, chemical determination of total $ZrO_2 + HfO_2$ was carried out. The colorimetric method with alizarin red was used, as proposed by Poluektov and Kononenko [8].

A correlation of results as obtained by the radiospectroscopic and chemical methods shows that divergence for 29 samples did not exceed ± 4%; it was below ± 10% for 16 samples, and over ± 10% in only 3 samples. The average divergence for 48 samples was ± 3.9%.

The data tabulated show a wide variation in Zr-Hf content for the Lovozero massif rocks: from 0.07 to 2.31% for ZrO_2, and from 0.0015 to 0.057% for HfO_2, with the ZrO_2/HfO_2 ratio varying but slightly from 32 to 64 (average 42; Zr/Hf ratio as recomputed from oxides to elements is 37). The Zr/Hf ratio for the Lovozero massif rocks is lower than that for magmatic rocks, conditionally taken to be 50; it is also lower than that for granitoids of the Verkhiset intrusion [5] where it was found to be 40.

The low value of the Zr/Hf ratio for the Lovozero massif rocks is of significance, inasmuch as there is an opinion abroad (3, 6, 9] that the Zr/Hf ratio is higher for Zr minerals from nepheline syenites than for those from granitoid rocks.

The Lovozero nepheline syenites are considerably richer in Zr, not only as compared to other types of rocks but as compared to nepheline syenites from other massifs (with the exception of Greenland). The average Zr content for magmatic rocks, according to Vinogradov [10],

Table 1. Content of Zirconium and Hafnium in Rocks of the Lovozero Massif

No. of sample	Rock type	Formation	Chem. analysis ΣZrO_2+ $+HfO_2$	X-ray-spectral analysis			Discrepancy of chemical and X-ray spectral analysis, in %
				ZrO_2	HfO_2	$\frac{ZrO_2}{HfO_2}$	
			weight %				
1	2	3	4	5	6	7	8
Rocks of the first complex (miascitic)							
139	Even-grained nepheline syenite with biotite	Ninchurt v.	0.290	0.272	0.0078	35	1.9
183	Porphyritic nepheline syenite	Alluaiv v.	0.138	0.146	0.0042	35	4.2
66	Poikilitic nepheline syenite	Suoluaiv v.	0.205	0.201	0.0047	43	0.0
196	Poikilitic nepheline syenite with hydrosodalite and sphene	Alluaiv v.	0.100	0.112	0.0035	32	5.3
147/2	Poikilitic hydrosodalite syenite	Motchisuai River Valley	0.105	0.138	0.0030	46	14.7
Rocks of the second complex (basically agpaitic)							
187	Cordierite-urtite	Alluaiv v.	0.134	0.147	0.0033	44	5.6
14b	Cordierite-urtite with apatite	Karnasurt v.	0.127	0.136	0.0041	33	4.9
262	Urtite with loparite	Alluaiv v.	0.410	0.383	0.0112	34	1.9
26b	Leucocratic lujavrite	Karnasurt v.	0.125	0.134	0.0036	37	4.8
162/35	Leucocratic lujavrite	Kuftnyun v.	0.653	0.536	0.0124	43	8.7
92/35	Leucocratic lujavrite	Kuftnyun v.	0.164	0.174	0.0043	40	5.1
26	Mesocratic lujavrite	Karnasurt v.	0.362	0.353	0.0110	32	0.0
171/35	Mesocratic lujavrite	Kuftnyun v.	0.412	0.427	0.0104	41	3.0
59/35	Mesocratic lujavrite	Kuftnyun v.	0.546	0.556	0.0145	38	2.6
4/35	Mesocratic amphibolic lujavrite	Kuftnyun v.	0.142	0.157	0.0043	36	6.4
28	Melanocratic lujavrite	Karnasurt v.	0.416	0.455	0.0130	35	5.9
8	Amphibole lujavrite	Karnasurt v.	0.275	0.305	0.0087	35	6.4
264	Lujavrite with loparite	Alluaiv v.	0.650	0.601	0.018	34	2.3
253/3	Lujavrite with loparite	Vavnbed v.	0.410	0.450	0.0130	35	6.1
270/3	Malinite with loparite	Vavnbed v.	0.159	0.154	0.0034	45	0.5
143	Foyaite	Karnasurt v.	0.486	0.470	0.0110	43	0.5
144	Foyaite	Karnasurt v.	0.432	0.417	0.0085	49	1.5
16/35	Foyaite with murmanite	Kuftnyun v.	0.096	0.074	0.0018	41	11.8
29/35	Foyaite with murmanite and eudialyte	Kuftnyun v.	0.184	0.167	0.0031	54	3.9
40/35	Foyaite with murmanite and loparite	Kuftnyun v.	0.097	0.071	0.0015	47	14.5
242/35	Foyaite with murmanite-lomonosovite	Kuftnyun v.	0.257	0.252	0.0049	35	3.8
230/35	Foyaite with lamprophyllite and murmanite	Kuftnyun v.	0.145	0.152	0.0044	35	3.8
202/35	Foyaite with lamprophyllite	Kuftnyun v.	0.130	0.133	0.0034	39	2.4
9/35	Foyaite with eudialyte	Kuftnyun v.	1.658	1.544	0.0317	49	2.5
248/35	Foyaite with eudialyte	Kuftnyun v.	1.660	1.660	0.0490	34	1.5
Rocks of the third complex (agpaitic)							
160	Eudialytic lujavrite	Alluaiv v.	1.112	0.970	0.0270	36	5.4
245	Eudialytic lujavrite	Alluaiv v.	1.52	1.570	0.0360	44	2.7
21/49	Eudialytic lujavrite	Alluaiv v.	1.350	1.280	0.0290	44	1.5
19/49	Eudialytic lujavrite	Alluaiv v.	1.200	1.169	0.0290	40	0.0
39/3	Eudialytic lujavrite	Chinglusuai River valley	2.410	2.310	0.0570	41	0.9
246	Porphyritic juvite with loparite	Alluaiv v.	1.320	1.190	0.0300	40	3.9
263	Porphyritic lovozeritic lujavrite	Karnasurt v.	1.610	1.580	0.0340	46	0.0
No. 2	Porphyritic lovozeritic lujavrite	Karnasurt v.	1.740	1.640	0.0360	46	1.9
93/4	Porphyritic lovozeritic lujavrite	Upper Elemaraik River	1.230	1.250	0.0280	45	1.9
22/49	Porphyritic lujavrite with murmanite	— —	0.840	0.948	0.0250	38	7.3
XXI	Porphyritic lujavrite with murmanite	Flora v.	1.350	1.260	0.0250	50	2.6
106	Porphyritic lovozéritic lujavrite with lomonosovite	Vavnbed v.	1.54	1.510	0.0350	43	0.0
477/5	Porphyritic lujavrite with murmanite and lamprophyllite	Muruai R. valley	1.580	1.740	0.0425	41	6.0

Table 1. Content of Zirconium and Hafnium in Rocks of the Lovozero Massif (Continued)

No. of sample	Rock type	Formation	Chem. analysis ΣZrO_2+HfO_2	X-ray-spectral analysis			Discrepancy of chemical and X-ray spectral analysis, in %
				ZrO_2	HfO_2	$\frac{ZrO_2}{HfO_2}$	
				weight %			
1	2	3	4	5	6	7	8
141	Poikilitic sodalite syenite	Chinglusuai R. valley	0.275	0.281	0.0088	32	2.6
1	Poikilitic sodalite syenite	same	0.149	0.120	0.0031	39	9.5
266	Poikilitic sodalite syenite	Tulbnnuai R.	0.146	0.138	0.0038	36	2.0
430	Tavite	Upper Tavaiakh R.	0.264	0.281	0.0074	38	4.4
3	Eudialyte	Vavnbed v.	8.670	8.200	0.2170	38	1.5
	Average						±3.9%

is: for acid rocks, 0.02%; intermediate rocks, 0.026%; basic rocks, 0.01%; ultrabasic rocks, 0.003%.

Average content of Zr in nepheline syenites, according to Johannsen [11], is 0.15% ZrO_2, but it is considerably higher in the Lovozero massif, probably as high as about 0.58% ZrO_2 and 0.014% HfO_2. The average content of ZrO_2 in rocks of complex I, Lovozero massif, is 0.167% complex II, 0.290%; and complex III, 1.49%. Rocks of complex I account probably for no more than 1% of the total volume of the massif; complex II, for about 75%; complex III, for about 24%.

Miascite rocks of complex I have the lowest Zr content in the Lovozero massif; agpaitic rocks of complex III - the highest. No relationship has been established for agpaitic rocks of both the second and third complexes, between the Na and K content on one hand and Zr and Hf content, on the other. For instance, cordierite-urtites, which are the most enriched by Na and K (complex II), have little Zr, and correspondingly little Hf. Low Zr and Hf content has been found in agpaitic rocks of complex III rich in sodalite; in a poikilitic sodalite syenite. No increase in Zr and Hf concentration has been observed in Lovozero agpaitic rocks, with an increase in alkali content.

The mineral zircon is absent in agpaitic rocks of the Lovozero massif, the bulk of Zr being concentrated in Zr-silicates (chiefly eudialyte lovozerite, etc.). This probably is explained by the fact that with the excess of alkalis over Al in these rocks, the alumina deficiency is compensated for by Fe, with the formation of aegirine and arfvedsonite; or by Ti and Zr, with the formation of titano-zirconium-silicates. Ti-silicates (lomonosovite, murmanite, etc.) commonly carry small amounts of Zr; and Zr-silicates (eudialyte, etc.) carry Ti. Isomorphism of quadrivalent Zr and Ti is possible in these minerals.

SUMMARY

1. The content of Zr and Hf in the Lovozero massif rocks varies widely, from 0.07 to 2.31% for ZrO_2, and from 0.015 to 0.57% for HfO_2, whereas the ratio of the two varies but slightly.

2. The accumulation of Zr and Hf takes place in late differentiates. Thus the average content of ZrO_2 in rocks of complex I is about 0.167%; complex II, 0.29%; complex III, 1.49%.

3. Agpaitic rocks of the massif (complexes II and III) are richer in Zr and Hf than the miascite rocks of complex I, although no relationship has been observed between the alkalies (Na and K) and Zr and Hf, in this massif.

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DISTRIBUTION OF RARE ELEMENTS IN MINERALS OF RARE-METAL GRANITE PEGMATITES

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Abstract

The contents of Li, Rb, Cs, Be, Ta and Nb in minerals of rare-metal granit pegmatites have been studied. The average content of tantalum and niobium in these minerals (from veins rich in rare elements) does not exceed 0.0003%; lithium, 0.018%; cesium, 0.107%; and the rubidium content reaches 0.64%. The dispersion of rare elements is chiefly determined by four factors: 1) the crystal-chemical properties of the rare elements, 2) their concentration, 3) the chemical character of the medium, and 4) the presence of favorable crystal structures in the form of such minerals as mica, tourmaline, beryl, among others.

In granite pegmatites, nearly all the rare elements either form independent rare-metal minerals or are found as admixtures among the principal, secondary, and other minerals. The ratio of these two modes of occurrence for rare elements in pegmatites is not only of theoretical but also of great practical interest, inasmuch as the overall content of a rare element in pegmatite is established in the analyse of samples from a pegmatite body, whereas only that part confined to the rare-metal mineral is actually extracted.

The content in pegmatite minerals, of such rare elements as Li, R Cs, Be, Ta and Nb, has been studied by many workers. However, the ratio of scattered Be to Be concentrated in Be minerals (chiefly beryl was tentatively calculated by A. A. Beus [1]. This paper is an attemp to arrive, on the basis of a detailed study of zonal pegmatites, at a quantitative estimate of the ratio of scattered to concentrated modes o occurrence for the rare elements listed above.

The rare-mineral content in various minerals was determined by quantitative spectroscopic and chemical analyses of pure monomineralic fractions selected under a binocular microscope. Samples were taken by zones, since it had been previously found [2] that the rare-element content is different for the same mineral from different zone Some 1 to 8 samples of each mineral were analyzed for each zone, depending on distribution, and an average was taken for each zone.

The quantitative mineral composition for each zone was determine visually, on the basis of detailed geological description of mine works and drillholes. For one of the veins, as described below, sketches were used, on 1:50 scale, of an artificially exposed area of over

12,000 m^2; another vein was documented by over 50 drillholes (with 90-98% core recovery), not counting sketching of trenches. The content in zones, of such rare-metal minerals as beryl, pollucite, and spodumene, was tabulated, with consideration given to the exploratory test data for Be, Cs, and Li.

A comparison of the visual method of determination of main rock-forming minerals with the results of tabulation of the chemical analysis of combined samples, has shown but a very slight divergence, some 3-5%. A correlation of several mineral contents with the results of a precise mineralogical analysis by E. F. Zif (oral communication) in the study of ore enrichment, has proved satisfactory. For instance, the quartz content in a vein, 25.5% by our data, compares with 25.2% as obtained by the mineralogical analysis; for muscovite it is 3.2 and 3.8%, respectively, etc.

The extent of zones was determined from the areas of their outcrops on large scale maps and cross-sections by conventional methods of volumetric reserves estimate, with the difference that, for our purposes, a relative rather than absolute volume was adequate, as expressed in per cent.

Given the content of a rare element in minerals, and the distribution of the minerals in a zone, computation of the average content of that portion of the rare element scattered throughout the zone presents no difficulties: with the distribution of zones and the average content in a zone of the scattered portion of the element thus determined, the average content of the scattered portion in a vein can be found.

Correlating the average content of the scattered portion of a rare element with its overall content in pegmatite, from the reserve estimate, we arrive at the ratio of scattered to concentrated form of occurrence for rare elements.

The scattering of rare elements on several pegmatite bodies in the Kola Peninsula and Mongol Altai was studied; data from two well-studied veins were used. Vein No. 1 (Kola Peninsula) was used for the determination of the degree of scattering for Li, Rb, Cs, Ta, and Nb; vein No. 2 (Mongol Altai) was used to compute Be. Both veins are identical in mineral composition.

Vein No. 1 is a gently dipping, rather thin body accompanied by numerous apophyses. Its texture is asymmetrically zonal. The asymmetry is revealed either in partial disappearance of some zones at the hanging or foot wall, or in different thicknesses of the same zone at different sides. From the edges to the center the composition of the pegmatite body is as follows:

1. Zone of a coarse tabular albite, with quartz, microcline, and spodumene.
2. Zone of quartz-albite-spodumene.
3. Zone of albitized blocky microcline, locally with apographic structures.
4. Zone of granular quartz-albite with spodumene.

5. Central zone of rare-metal replacement, with pollucite, rose spodumene, and other rare-metal minerals.

The vein is made up chiefly of quartz, albite, microcline, tourmaline, muscovite, pollucite, beryl; contents throughout the zones are given in Table 1. The vein contains spodumene, lepidolite, montebrasite, and lithiophilite of the Li minerals. Also present are apatite, garnet, simpsonite, and other minerals in very small quantities (less than 0.1-0.3%) and therefore not accounted for, mainly because of their comparatively low content of scattered rare elements.

Li content in minerals was determined by quantitative spectrometri analyses (L. D. Sazhina, analyst). Table 1 gives the content of scattere Li in zones of vein No. 1. Table 3 shows the average content of scattered Li throughout the vein as a whole (0.018%). The average overall

Table 1. Calculations for the Average Content of Dispersed Lithium in Zones of Vein No. 1

Mineral	Content of mineral in zone, %	Content of lithium in mineral, %
Zone of tabular albite		
Albite	63	0.003
Microcline	11	0.006
Quartz	20	0.003
Tourmaline	5	0.02
Muscovite	1	0.03
Total	100	
Average for zone		0.004
Quartz-albite-spodumene zone		
Microcline	7	0.006
Albite	26	0.003
Quartz	58	0.003
Tourmaline	1.5	0.02
Muscovite	6	0.03
Beryl	1.5	0.42
Total	100	
Average for zone		0.011
Microcline-block zone		
Albite	12	0.02
Microcline	75	0.037
Quartz	12	0.003
Muscovite	1	0.05
Total	100	
Average for zone		0.029
Granular quartz-albite zone		
Albite	50	0.02
Microcline	16	0.039
Quartz	29.6	0.003
Muscovite	3	0.1
Beryl	0.4	10.48
Pollucite	1	0.14
Total	100	
Average for zone		0.013
Zone of rare-metal mixtures		
Albite	36	0.02
Microcline	20	0.039
Quartz	33	0.003
Tourmaline	1	0.64
Muscovite	5.5	0.1
Beryl	0.5	0.48
Pollucite	4	0.14
Total	100	
Average for zone		0.039

content of Li in the vein is 0.45%, according to the reserve estimate by Ya. Kh. Eselev and V. P. Zueva. Accordingly, the scattered state comprises but 0.018/0.45 · 100 = 4% Li. The balance of about 96% is tied up in Li minerals; chiefly in spodumene, less so in lepidolite and montebrasite, and to a much smaller extent in purpurite, lithiophilite, and others.

Cesium content in more common Cs-minerals was determined by quantitative spectrometric analyses by T. F. Borovik-Romanova on the material collected by A. F. Sosedko [2]. Content of Cs_2O in beryl was determined chemically from our sample (Z. T. Kataeva, analyst). Content of Cs in quartz, albite, and spodumene, not recognized by the spectrometric method (N. V. Lizunov, analyst), was assigned conditionally; because of its low figure, it should not perceptibly affect the overall results.

The content of scattered Cs in the zones of coarse-tabular albite, quartz-albite-spodumene, and blocky microcline was taken from the results of exploratory tests. Since no pollucite has been found in these zones, despite a painstaking macro and micro-study, it may be assumed that all Cs is in the scattered state.

The average content of scattered Cs in the remaining zones of granular quartz-albite and in the central zone of rare-metal replacement—where pollucite has been found—is given in Table 2. The average content of scattered Cs throughout the vein as a whole is given in Table 3; it is 0.107%. The average overall Cs content for the vein, according to reserve estimate, is 0.42%. Accordingly, 0.107/0.42 · 100, or about 25% of the Cs, is in the scattered state. The balance of it, over 75%, is tied up in pollucite.

Rb content in Vein No. 1 is 0.64%. Rb is known to be completely scattered throughout rock-forming minerals. According to the data of a quantitative spectrometric analysis of our samples (L. D. Sazhina, analyst), microcline contains 0.3-1.5% Rb; lepidolite, 0.2-2.7%; muscovite, 0.16-0.7%; beryl, 0.005-0.4%; pollucite, 0.14-0.58%; albite, up to 0.1%; spodumene, 0.001-0.36%; tourmaline, 0.01-0.72%; purpurite, 0.01%; montebrasite, 0.01%.

Tantalum content in vein No. 1 is 0.022%, and niobium, 0.007%. These elements are fully concentrated in tantalite, simpsonite, microlite, stibiotantalite. This statement is based on the following facts. It is well known that Ta and Nb occur to a large extent only in minerals of Ti, Zr, W, Sn, U and Th, also in ferrous silicates (pyroxene, amphibole, biotite, etc.) represented in vein No. 1 only by cyrtolite and cassiterite—and that in negligible quantities, 0.03% and 0.004%, respectively (after E. F. Zif).

According to data by Rankama [4, 5], Ta and Nb content in feldspars, quartz, and spodumene (main components of vein No. 1) from granite pegmatites does not exceed $n \cdot 10^{-5}$, reaching $n \cdot 10^{-3}$ only in muscovite, tourmaline, and garnet; however, the total of the latter minerals in our pegmatite is only 6%.

The content of scattered Ta and Nb in vein No. 1 may be estimated

Table 2. Calculation for the Average Content of Dispersed Cesium in Zones of Vein No. 1

Mineral	Content of mineral in zone %	Content of cesium in mineral, %
Granular quartz-albite zone		
Albite	43	0.002
Microcline	14	0.17
Quartz	25	0.001
Lepidolite	1	0.30
Muscovite	2.6	0.17
Spodumene	14	0.005
Beryl	0.4	2.03
Total	100	
Average for zone		0.041
Zone of rare-metal mixtures		
Ablite	27	0.002
Microcline	16	0.17
Quartz	25	0.001
Lepidolite	5.5	0.30
Muscovite	4	0.17
Beryl	0.5	2.03
Spodumene	21	0.005
Tourmaline	1	0.025
Total	100	
Average for zone		0.063

at 0.0002 and 0.0003% of each (respectively), which gives the relative content of 0.0002 · 100/0.022 or about 1% for Ta and 0.0003 · 100/0.007 or about 4% for Nb; these elements are virtually fully represented by individual minerals.

The best available material for the determination of the degree of scattering for Be was found to be in vein No. 2 (Mongol Altai). It is a stock-like body, fairly thick, and having a well-defined concentric zonal texture. From the edges to the center, the vein is made up of the following zones, fringing one another:

1. Graphic pegmatite zone.
2. Zone of fine-grained albite, with beryllium.
3. Zone of coarse blocky microcline.
4. Quartz-muscovite zone.
5. Zone of quartz-cleavelandite-spodumene.
6. Central zone of blocky quartz with microcline blocks and a lepidolite lens.

The vein is made chiefly of albite, microcline, quartz, spodumene, muscovite, garnet, apatite, tourmaline, lepidolite; their distribution throughout the zone is given in Table 4. Beryl alone is developed, of Be minerals. Also present are lithiophilite, pollucite, tantalite-columbite, microlite, montebrasite, etc.; their development is very restricted (less than 0.1-0.2%), and they may be disregarded.

Beryllium content was determined chemically (S. N. Fedorchuk, analyst, A. A. Beus collection, limit of error 0.0002%). Table 4 gives the content of scattered Be, by zones, and Table 5 shows it for the vein as a whole (0.0009%). The overall content of Be in vein No. 3, according to the reserve estimate, is 0.016%. Accordingly, there is 0.0009/0.016 · 100 = 5.6% Be in the scattered state. The balance of it, or over 94%, is concentrated in beryl.

Thus the degree of scattering of various rare-elements throughout the rock-forming minerals of granite pegmatites, differs greatly; Ta and Nb are virtually un-scattered, since their average content in these minerals does not exceed 0.0003%; the average content of scattered Be

Table 3. Calculation for the Average Content of Dispersed Lithium and Cesium in Vein No. 1

Zone	Extent of zone	Content in zone, %	
		lithium	cesium
Tabular albite zone	28	0.004	0.094
Quartz-albite-spodumene zone	18	0.011	
Microcline-block zone	18	0.029	0.240
Granular quartz-albite zone	15	0.013	0.041
Zone of rare-metal mixtures	21	0.039	0.063
Total	100		
Average for vein		0.018	0.107

is comparatively low, being 0.0009%; it is as high as 0.018% for Li; 0.107% for Cs; for Rb, which is fully scattered, it reaches 64%.

The degree of scattering for rare elements appears to be determined by the following 4 main factors: 1) the crystallochemical properties of rare elements, 2) their concentration, 3) chemical character of the medium, 4) the presence of favorable crystalline structures of certain common minerals. Foremost among the crystallochemical properties affecting the degree of scattering for rare minerals is their ionic radii.

It is well known that the entry of elements into crystalline structures is predetermined to a considerable extent by the similarity of the ionic radii of isomorphous elements, and by their polarization features. If the ionic radii of a rare element and a rock-forming one are close, the rare element will tend to scatter throughout the minerals of the latter, as occurs with Rb which is fully scattered in K and Cs minerals.

However, Be and similar elements undergoes little scattering in rare-metal granite pegmatite, despite the similarity of ionic radius (0.34 Å) with that for Si^{4+} (0.39 Å). On the other hand, Cs with ion radius of 1.65 Å, considerably different from ionic radius (1.33 Å) for K, which is the closest to it among the common elements, is easily scattered in K minerals. It follows that the degree of scattering for rare minerals depends not only on the similarity of their ionic radii with those of widely distributed elements, but on other crystallochemical properties, as well.

More specifically, as shown in Table 6, scattering of rare elements increases on the whole, with the decrease of their EC (energy constant) and ionization potentials.

Obviously, such ions as Ta, Nb, Be, with high EC and ionization potentials, are characterized by a higher capacity to form their own minerals; therefore they scatter hardly at all, despite the presence of ions with similar radii. Conversely, ions which are characterized by low EC and ionization potentials, such as Rb and Cs, have but a weak tendency to form minerals of their own; therefore their scattering is

Table 4. Calculation for the Average Content of Dispersed Be in Zones of Vein No. 2

Mineral Mineral	Content of mineral in zone, %	Content of Be in mineral, %
Zone of albite altered graphic pegmatite		
Quartz	30	0.0002
Microcline	45	0.0005
Albite	20	0.0012
Muscovite	5	0.0032
Total	100	
Average for zone		0.0007
Fine-grained albite zone		
Quartz	5	0.0002
Microcline	47	0.0005
Albite	40	0.0012
Muscovite	6	0.0032
Garnet	1	0.0012
Apatite	1	0.0018
Total	100	
Average for zone		0.0009
Massive, block-microcline zone		
Quartz	12	0.0002
Microcline	85	0.0006
Muscovite	3	0.0032
Total	100	
Average for zone		0.0006

Mineral	Content of mineral in zone, %	Content of Be in mineral, %
Quartz-muscovite zone		
Quartz	55	0.0002
Cleavelandite	8	0.0012
Muscovite	35	0.0032
Garnet	1	0.0012
Apatite	0.5	0.0018
Tourmaline	0.5	0.0020
Total	100	
Average for zone		0.0014
Quartz-cleavelandite-spodumene zone		
Quartz	38	0.0002
Cleavelandite and albite	37	0.0018
Microcline	2	0.0010
Spodumene	20	0.0015
Muscovite	3	0.0046
Total	100	
Average for zone		0.0012
Block quartz with block-microcline and lepidolite lens		
Quartz	77	0.0002
Microcline	18	0.0010
Lepidolite	2	0.0050
Albite	2	0.0020
Spodumene	1	0.0015
Total	100	
Average for zone		0.0005

affected by the presence or absence of elements with similar ionic radii.

The concentration of a rare element in a melt-solution affects the degree of its scattering to the same extent in all instances: the scattering of a rare element increases with its concentration, as noted by Beus [1] for Be. The case of Cs is no less demonstrative. The amount of Cs in microclines from pegmatites low in Cs is 0.005-0.02%; it is about ten times higher for pegmatites high in Cs: 0.05-0.23%.

The effect of chemical character of a medium may be demonstrated in the instance of the same Be which is poorly scattered in granite pegmatites with excess of silica, while it is nearly completely scattered in

Table 5. Calculation of Average Content of Dispersed Be in Vein No. 2

Zone	Distribution of zone, %	Content of Be in zone, %
Zone of albite-altered graphic pegmatite	11	0.0007
Zone of fine-grained albite	11.4	0.0009
Zone of massive block microcline	35	0.0006
Quartz-muscovite zone	8	0.0014
Quartz-cleavelandite-spodumene zone	28.3	0.0012
Zone of block quartz with block microcline and lepidolite lens	6.3	0.0005
Total	100	
Average for vein		0.0009

alkaline rocks with deficiency of silica [3], where it replaces Si^{4+} in Si-O tetrahedrons.

The effect of chemical character of a medium is also well-demonstrated in heterovalent isomorphism which requires not only the similarity of ion radii for the isomorphous elements but also the presence of cations capable of compensating the electrostatic balance disturbed by the replacement of a common element by a rare element.

Finally, a peculiar "hospitality" of certain minerals for rare elements should be noted. Thus micas are always marked by a higher content of nearly all rare minerals; the same is true for tourmalines.

Table 6.

Elements	S_1 weight-content,%	S_2 Average mineral content of dispersed elements, %	$\frac{C_2}{C_1} \cdot 100$ relative dispersion, %	EC*	Ionization potential
Ta	0.022	0.0003	1.0	12.2	55
Nb	0.007	0.0003	4.0	12.2	50
Be	0.016	0.0009	5.6	2.65	18.12
Li	0.45	0.018	4.0	0.74	5.36
Gs	0.42	0.107	25.0	0.42	3.87
Rb	0.64	0.64	100.0	0.43	4.16

*From the editors: EC, or "energy constant", developed by A. E. Fersman, is an energy equivalent introduced by an ion when it enters a crystalline lattice, and is expressed by the formula $EC = \frac{W^2}{2r_i}$, where W = valence, and r_i = ionic radius.

No less remarkable is beryl, which is capable of selective capture of sizable amounts of Cs. The presence of such crystal structures natur ally facilitates the scattering of specific rare elements.

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